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# Sealing Glasses for Electrochemical Devices

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# Sealing Glasses for Electrochemical Devices

Richard K. Brow  
Missouri S&T

**IMI Conference on Functional Glasses:  
Properties and Applications  
for Energy and Information**

January 8, 2013  
Siracusa, Sicily, Italy

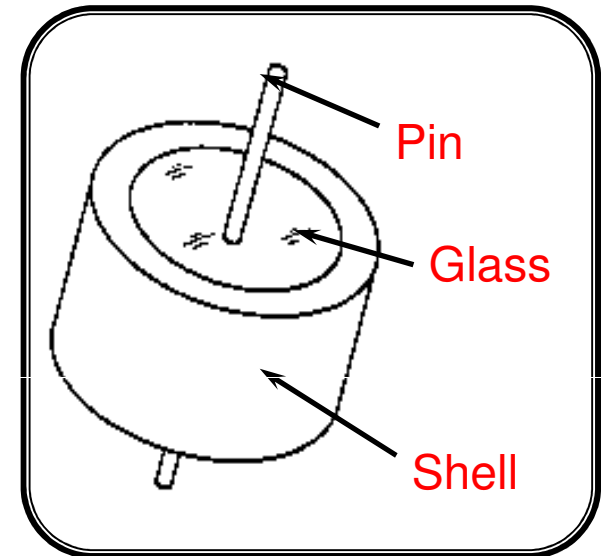


# Outline

- Background- and opportunities
  - *Low volume, high value technologically enabling glasses*
- Ambient temperature devices
- Na/ $\beta$ -Al<sub>2</sub>O<sub>3</sub> batteries
- Solid oxide fuel cells
- What's next?
  - Research focus areas

# Function and requirements of hermetic seals

- Isolate components from environment
- Mechanically bond different components
- Electrically insulate one component from another
- Weak link/strong link functions
- Thermo-mechanical compatibility
  - CTE requirements (matched vs. compression)
  - Sealing temperature
- Environmental stability (ambient and other component materials)
- Component functionality (dielectric, optical, etc. properties)

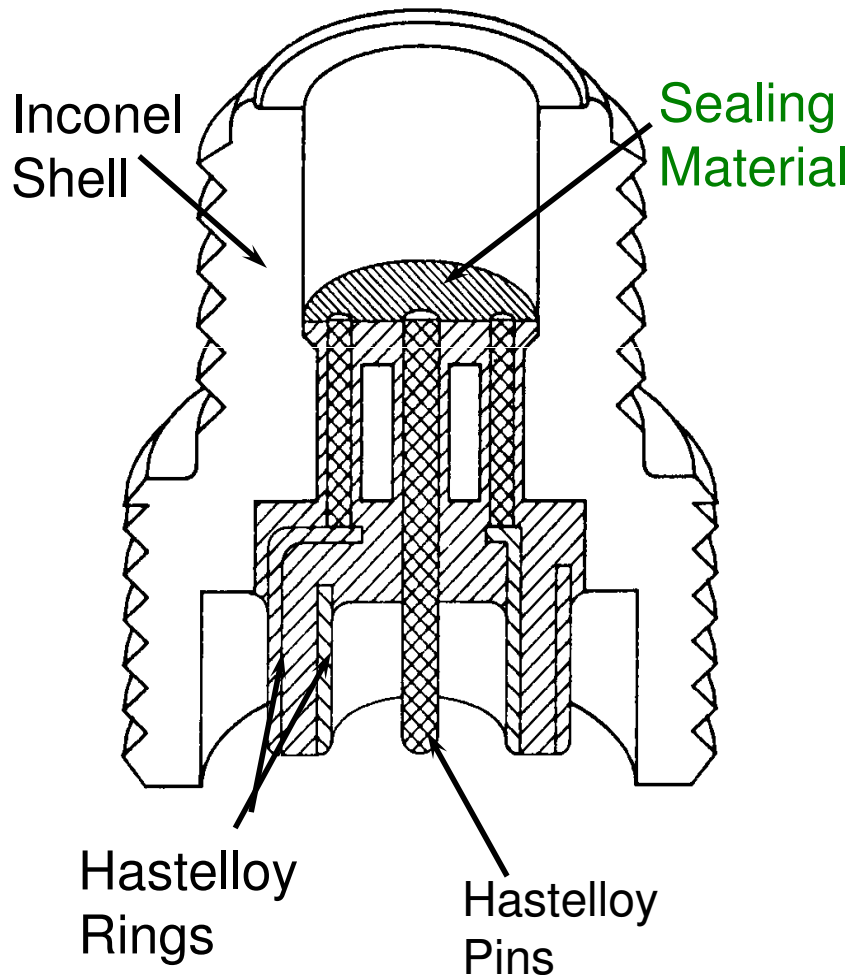




## Why use glasses for hermetic seals?

- Superior hermeticity
  - $>10^3$  lower permeation rates than polymers
- Compositional flexibility to tailor specific properties
  - E.g., CTE ranges to match fused silica and copper....
- High temperature stability
- Electrically insulating
- Processing flexibility
  - Viscous flow for complex shapes
  - Solid, powder preforms; thin films
  - Glass-ceramic options
- Brittle- CTE mismatches
- Temperature limitations
- Incompatible chemistries

# Example: High-strength seals for pyrotechnics



- High yield strengths
  - >100 kpsi
- good fracture toughness
- excellent corrosion resistance

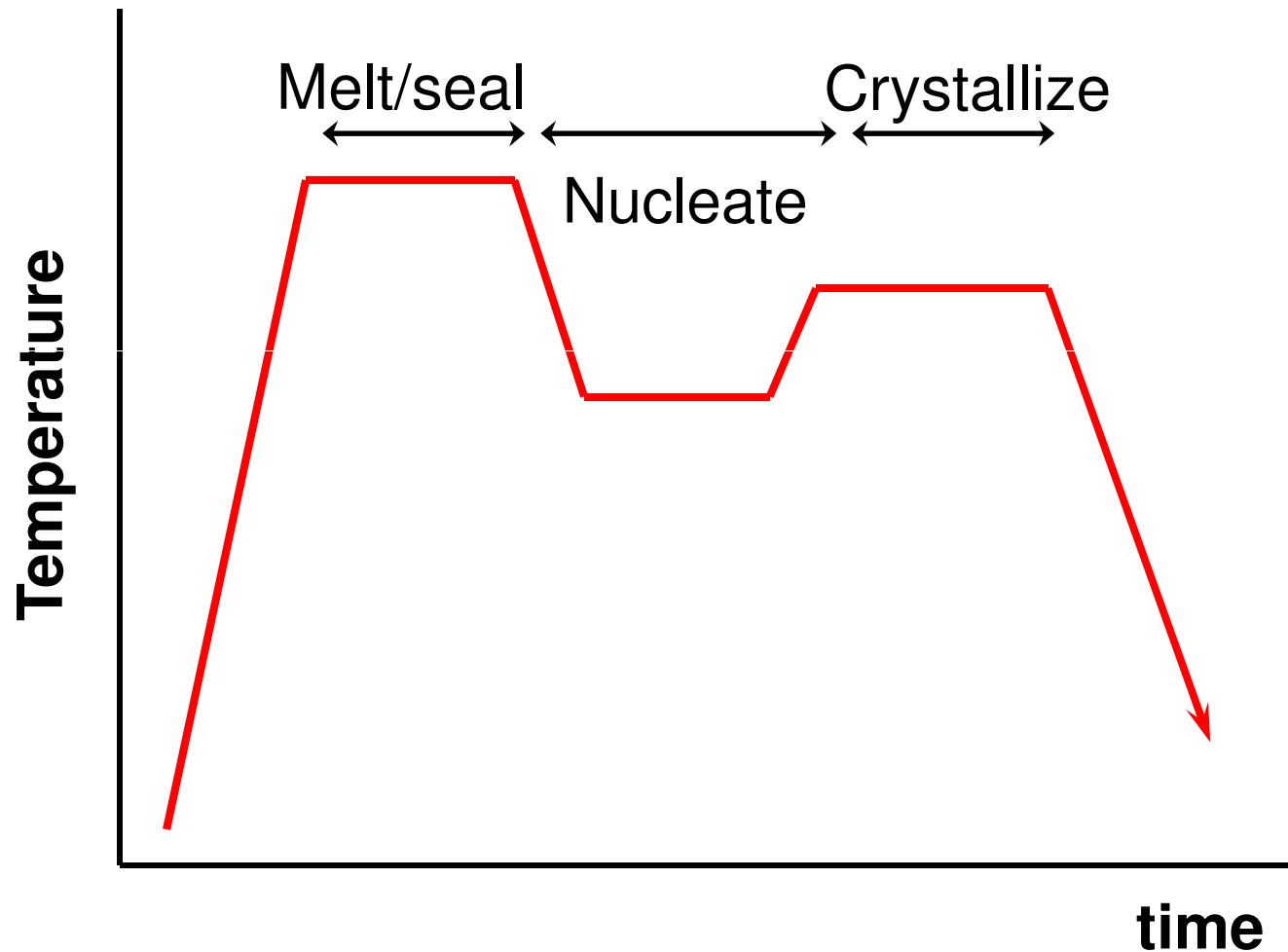
## Problem:

Hermetic seals are required to isolate air-sensitive materials.

## •Glass-ceramics are the solution

- good mechanical properties
- CTE-matches to many alloys
- good chemical properties
- convenient manufacturing

# Conventional glass-ceramic process profile



# Li-silicate glass ceramics have the requisite CTEs for super-alloy seals

'S-glass' (mole%)

**23.7 Li<sub>2</sub>O** **2.8 K<sub>2</sub>O** **2.6 Al<sub>2</sub>O<sub>3</sub>**  
**2.6 B<sub>2</sub>O<sub>3</sub>** **1.0 P<sub>2</sub>O<sub>5</sub>** **67.1 SiO<sub>2</sub>**

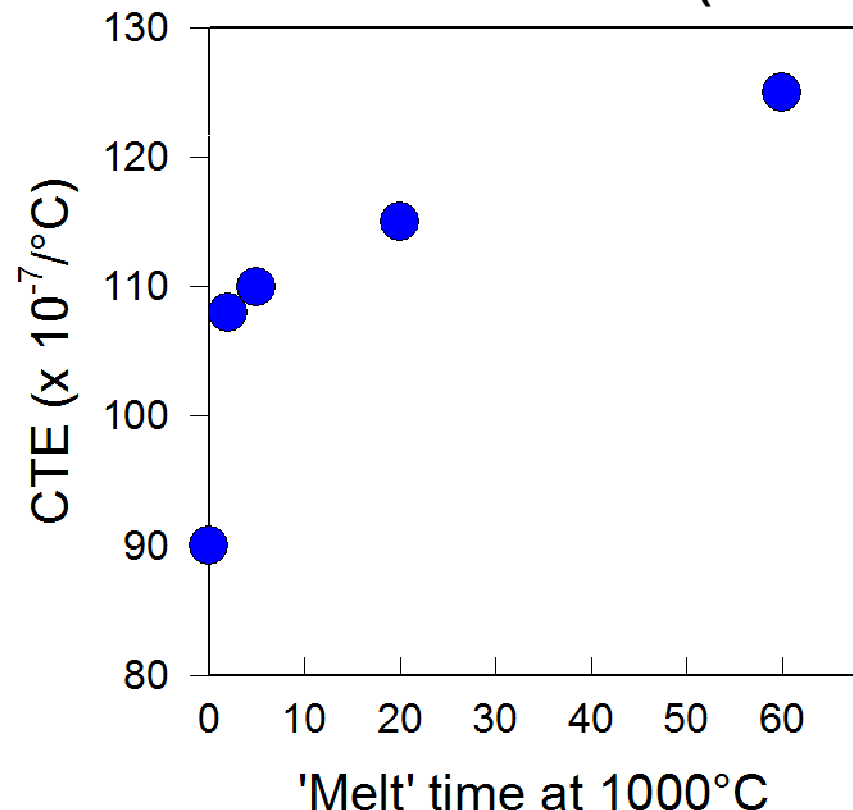
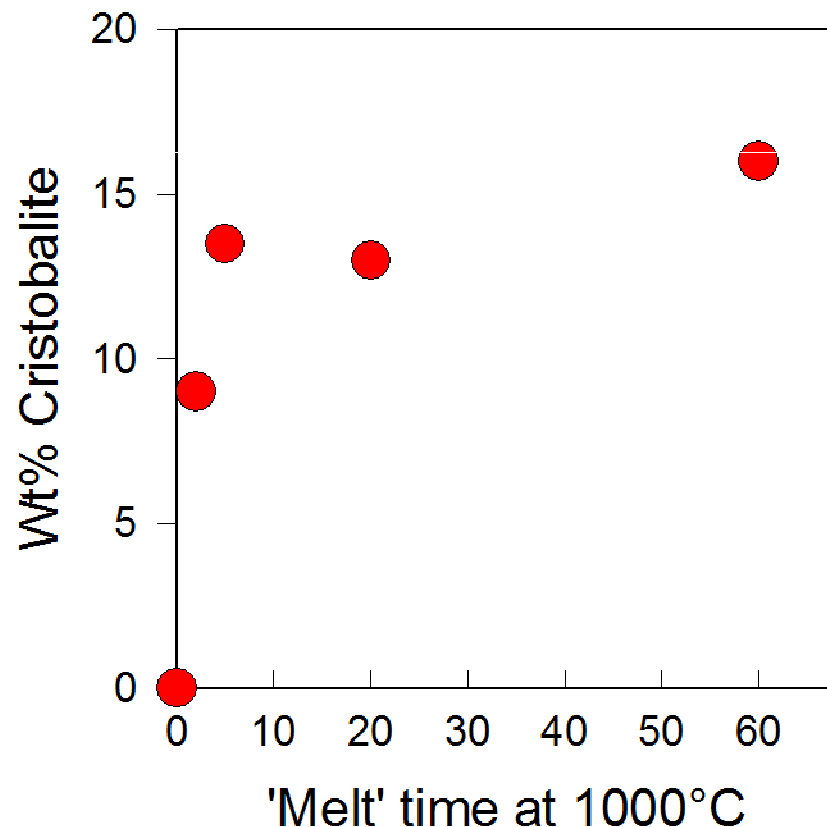
CTE depends on crystalline phases:

Li-disilicate,  
cristobalite,

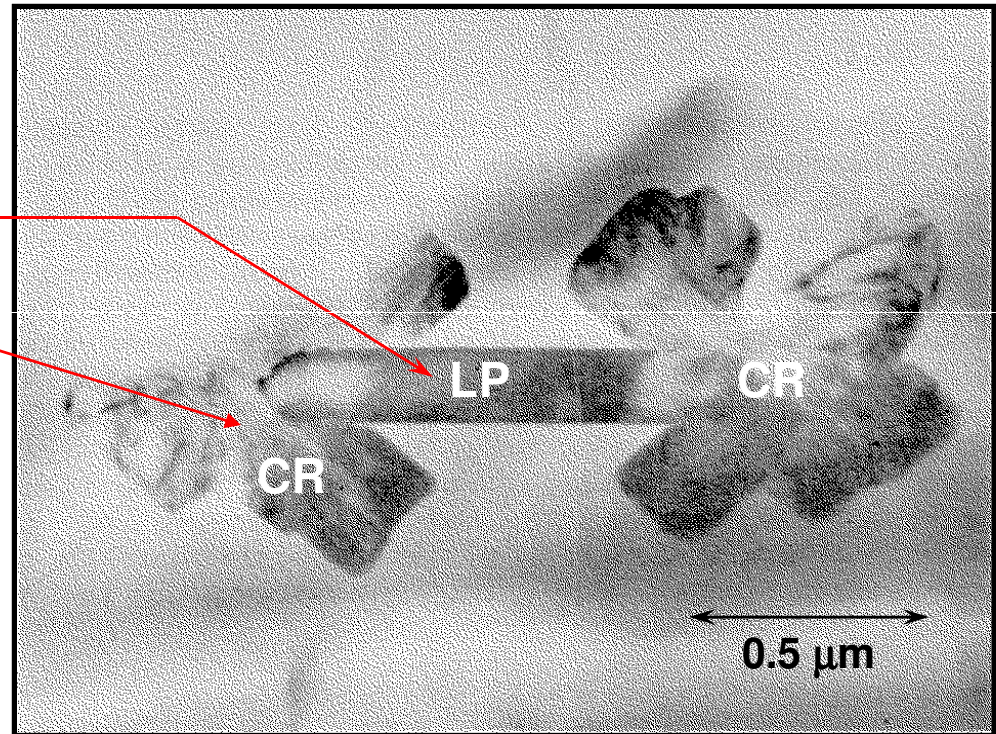
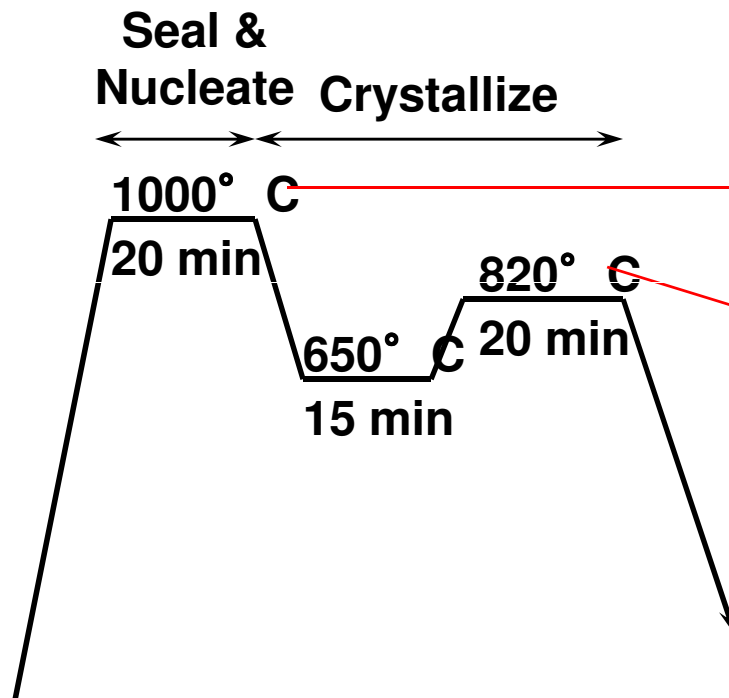
CTE  $\sim 110 \times 10^{-7}/^{\circ}\text{C}$

CTE  $\sim 125 \times 10^{-7}/^{\circ}\text{C}$  (20-100 $^{\circ}\text{C}$ )

$\sim 500 \times 10^{-7}/^{\circ}\text{C}$  (20-300 $^{\circ}\text{C}$ )



# High temperature heterogeneous nucleation leads to desirable glass-ceramics

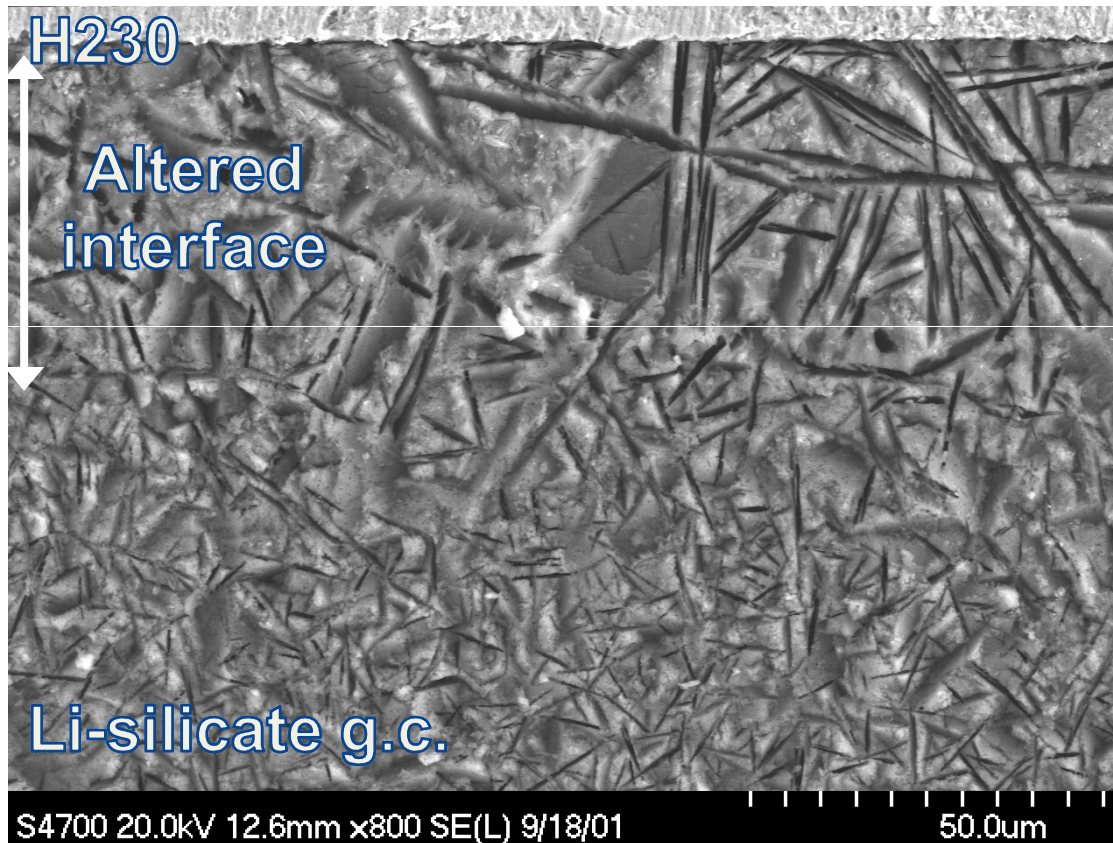


- $\text{Li}_3\text{PO}_4$  nuclei form at 1000° C
- Epitaxial growth of cristobalite at 820° C
  - no nuclei: low CTE Li-disilicate

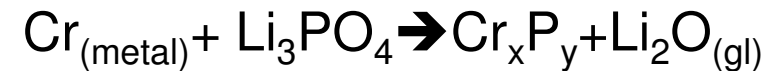
(Headley and Loehman, J. Am. Ceram. Soc., 1984)



# The heterogeneous nucleation mechanism has important application ramifications



- poorly crystallized interface
- Cr-phosphide crystallites



- 25% lower CTE

detonators, actuators, bolt cutters, high-voltage connectors, etc.

## Materials issues for designing a sealing glass

- CTE requirements
- Other desirable physical and chemical properties
- Sealing and operational temperatures
  - Viscosity and process-required properties
  - Long-term stability of properties
  - Interactions with seal components

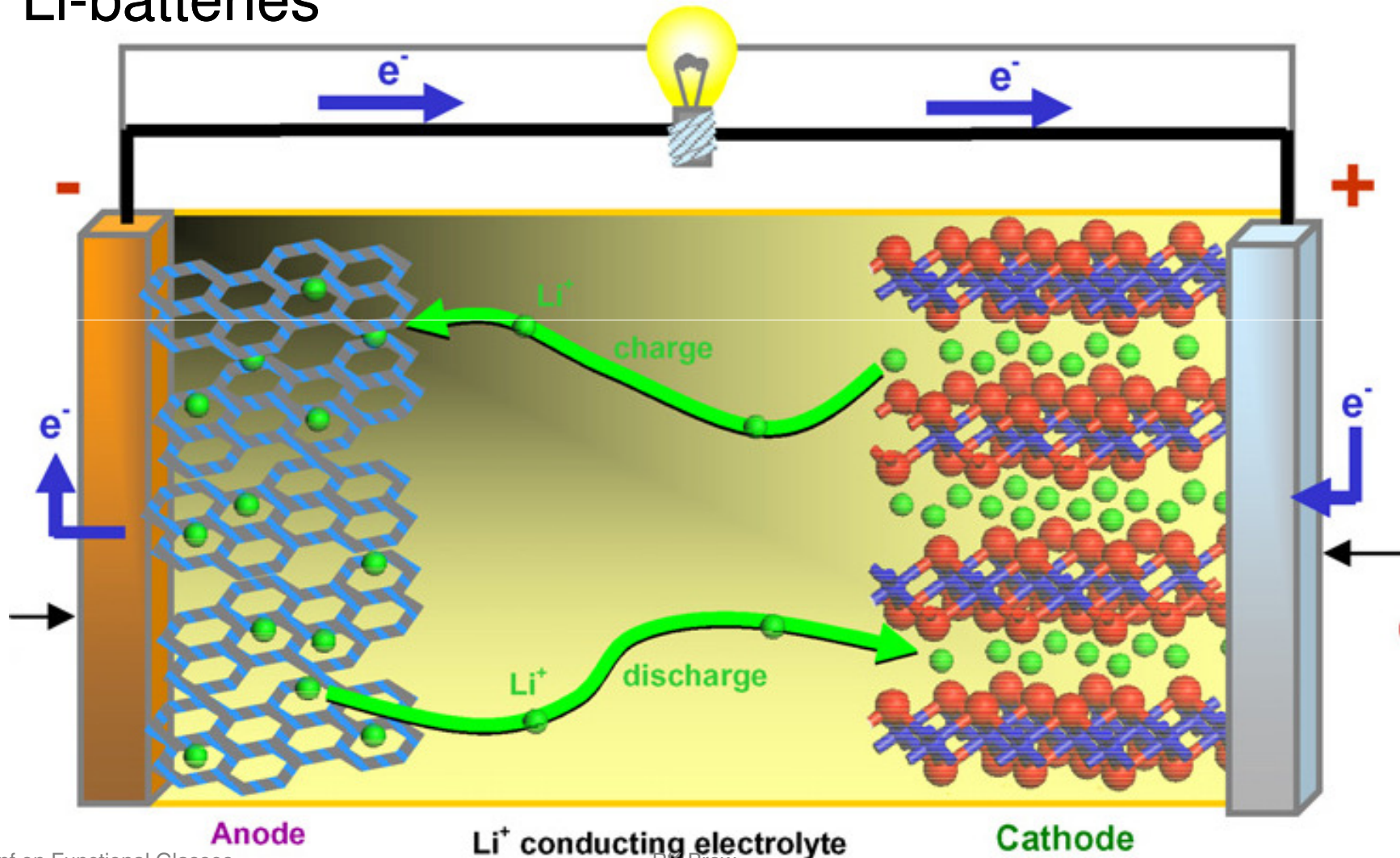
## We will consider three types of electrochemical devices

- Lithium batteries (ambient temperatures, liquid electrolyte)
  - Lithium stability
- Alkali storage batteries (intermed. temperatures, 200-400° C)
  - Long-term alkali stability
- Solid oxide fuel cells (high temperatures, 600-900° C)
  - Long-term thermo-chemical stability
  - Failure from thermal cycling

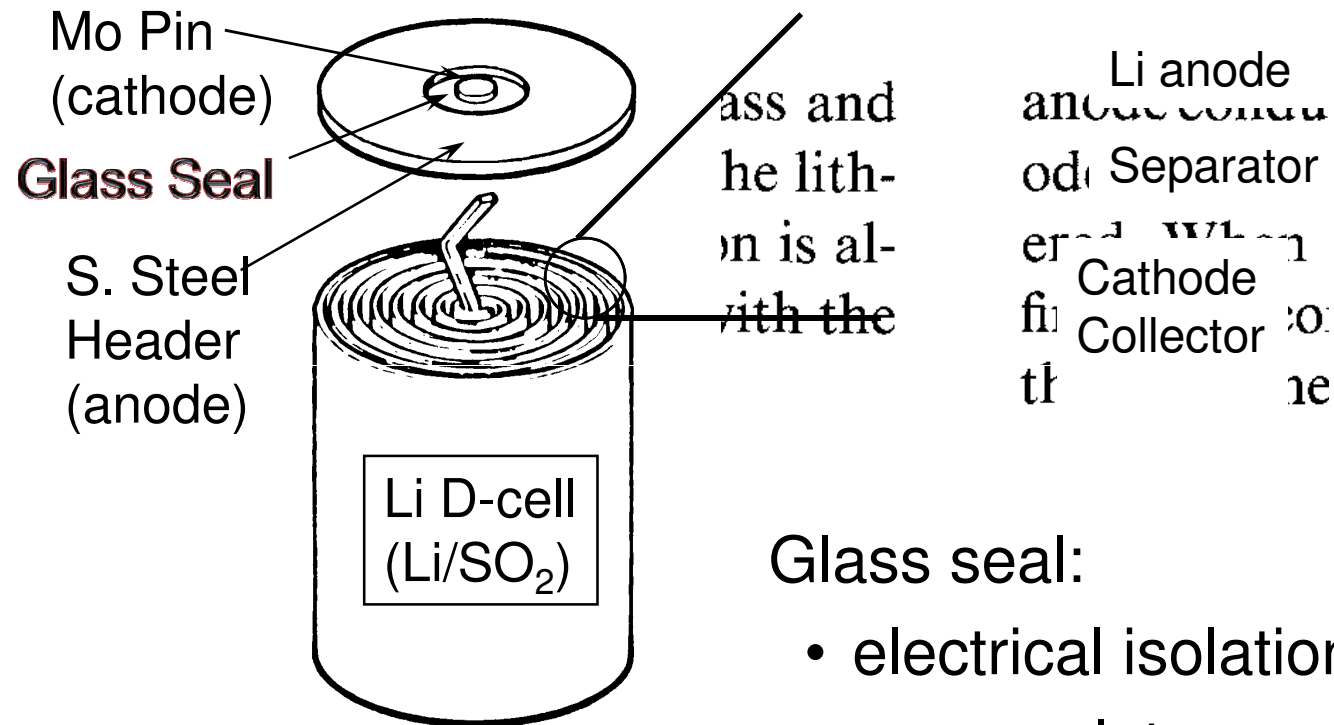
***Glass is an enabling technology to produce robust devices***



Glasses have been developed as electrolytes for Li-batteries



## Example: Lithium D-cell

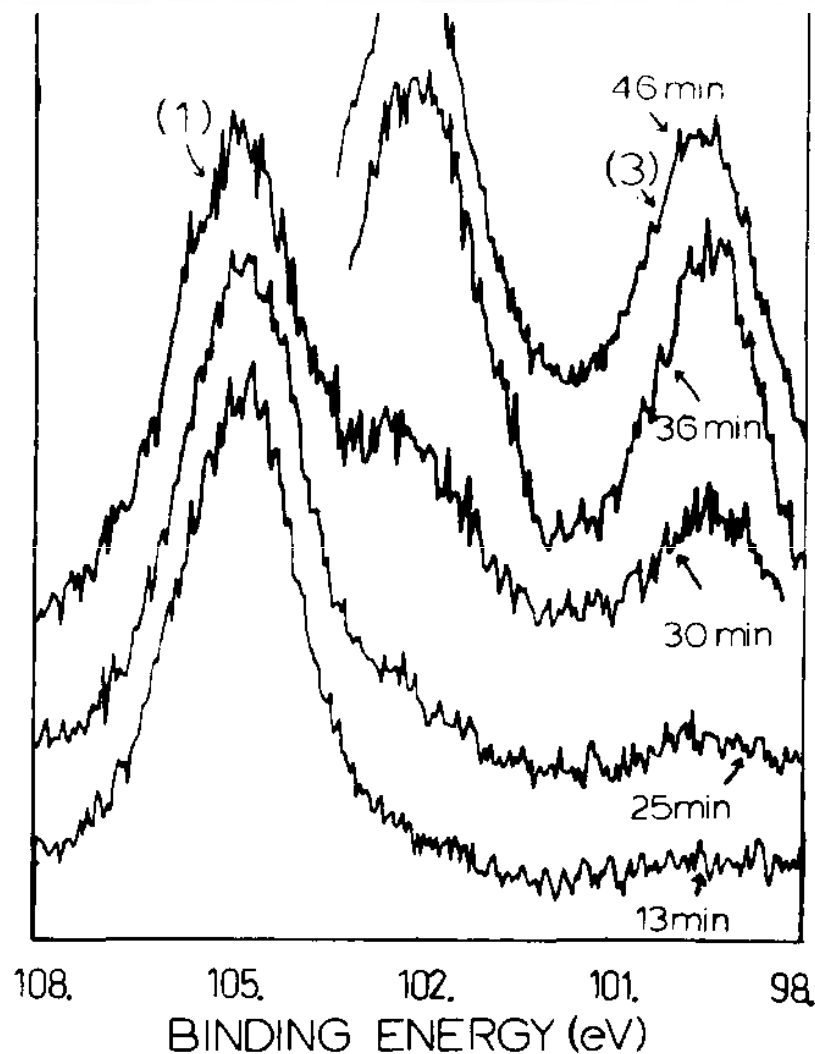


### Glass seal:

- electrical isolation
- encapsulates reactive electrolyte

# Lithium and other alkali metals react with silicate glasses

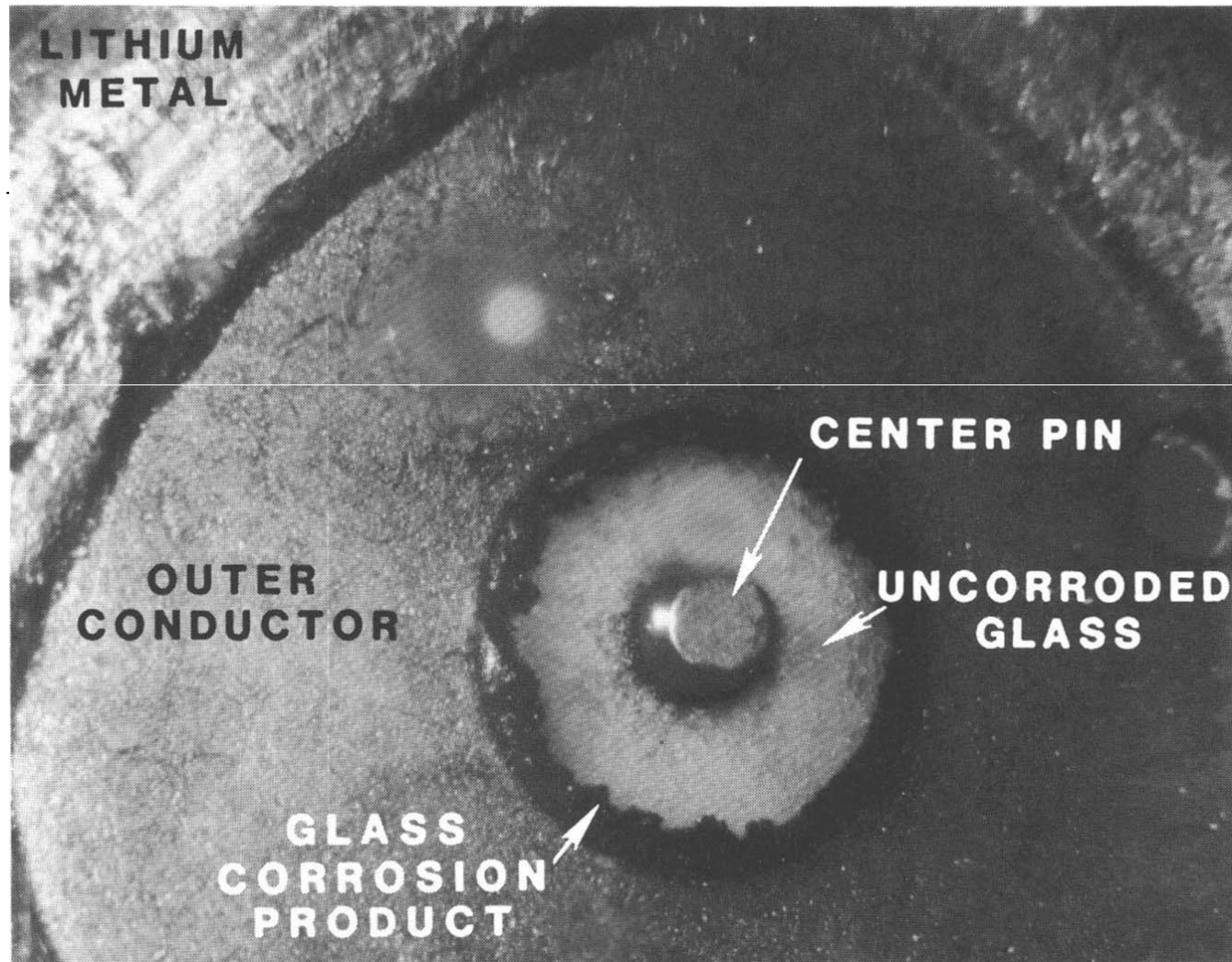
Li thin film on silica at 75° C



Maschoff, et al., Appl. Surf. Sci. 27 (1986) for Li/SiO<sub>2</sub> heated to 75° C for given times after



## Silicate glass seals are attacked by lithium

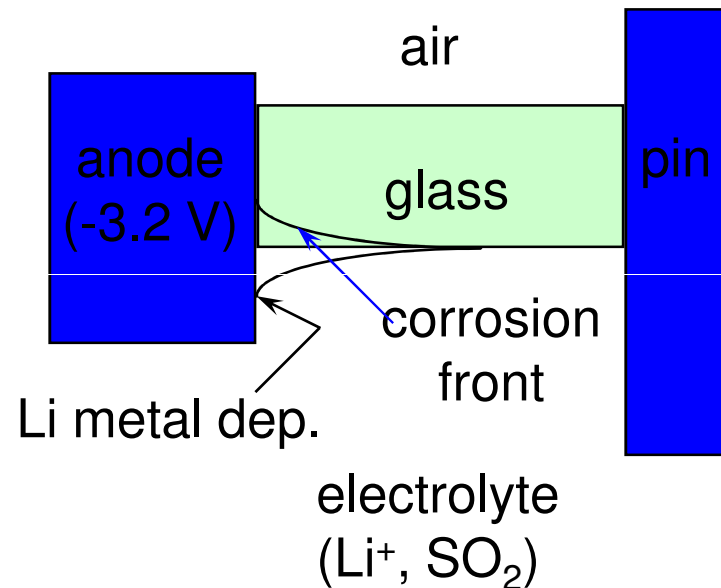


Conventional  
silicate sealing  
glass after three  
months at 70° C,  
Li/SOCl<sub>2</sub>  
electrolyte-

Bunker et al., J.  
Mat. Res. 2 (1987)

A mechanism for glass corrosion has been established

### Underpotential Deposition



Reaction limits the shelf-life of Li liquid electrolyte cells



(Bunker *et al.*, *J. Mater. Res.*, 1987.)

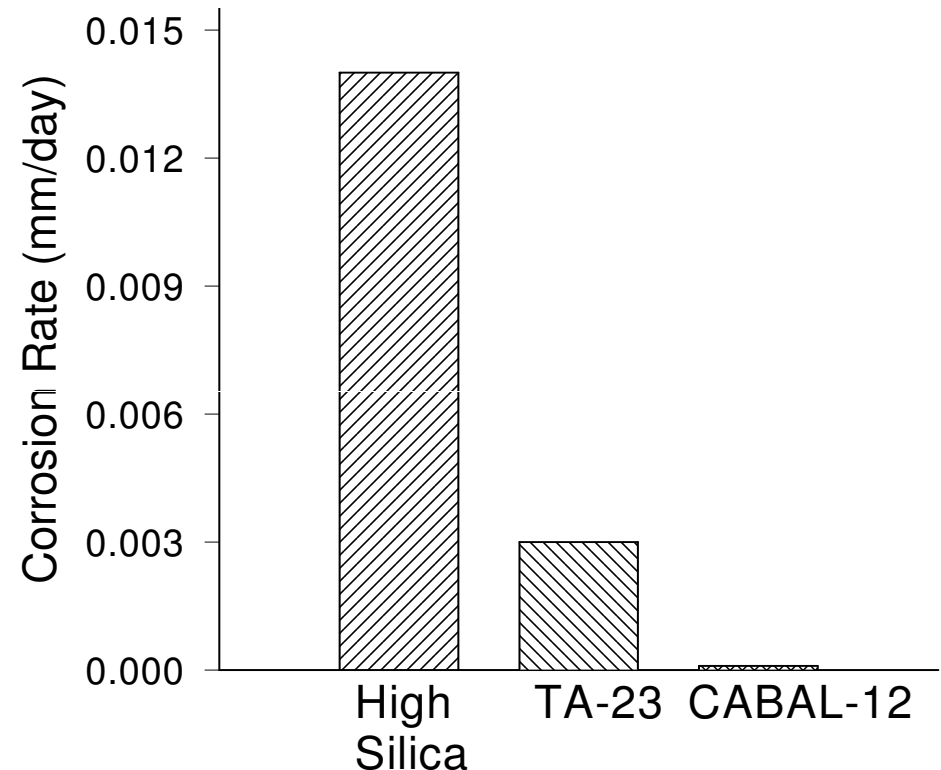
# Corrosion resistant glasses have been developed

## 1. Low silica compositions

- **TA-23** (45 wt%  $\text{SiO}_2$ )
  - shelf-life > 5 years

## 2. Aluminoborate compositions

- **CABAL-12** (silica-free)
  - $20\text{MgO} \cdot 20\text{CaO} \cdot 20\text{Al}_2\text{O}_3$ 
    - $40\text{B}_2\text{O}_3$
  - shelf-life > 20 years
  - lower sealing temperature
  - less prone to crystallization



Applications include Li-batteries for cameras, computers, and biomedical components.

These glasses are used in designs for long-life Li cells

# United States Patent

Howard et al.

(10) Patent No.: US 7,803,481 B2

(45) Date of Patent: Sep. 28, 2010

LITHIUM-ION BATTERY

# United States Patent

Howard et al.

(10) Patent No.: US 7,641,992 B2

(45) Date of Patent: Jan. 5, 2010

MEDICAL DEVICE HAVING LITHIUM-ION  
BATTERY

4,446,212 A 5/1984 Kaun  
4,464,447 A 8/1984 Lazzari et al.

# United States Patent

Larson et al.

(10) Patent No.: US 6,498,951 B1

(45) Date of Patent: Dec. 24, 2002

IMPLANTABLE MEDICAL DEVICE  
EMPLOYING INTEGRAL HOUSING FOR A  
FORMABLE FLAT BATTERY

5,199,428 A 4/1993 Obel et al. .... 128/419 C  
5,207,218 A 5/1993 Carpentier et al. ... 128/419 PG  
5,312,453 A 5/1994 Shelton et al. .... 607/19

# United States

# Patent Application Publication

Lasater et al.

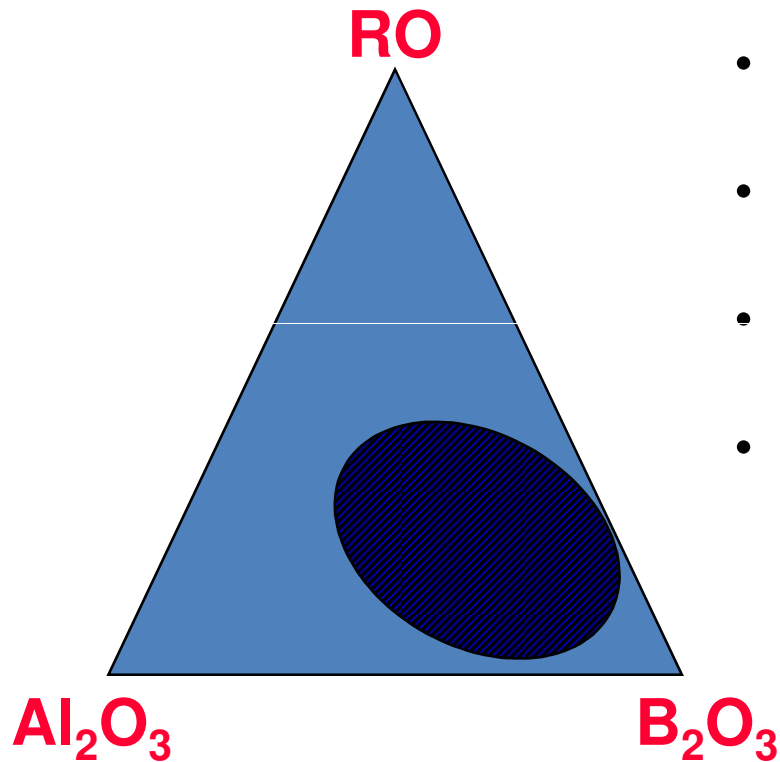
(10) Pub. No.: US 2005/0255380 A1

(43) Pub. Date: Nov. 17, 2005

LITHIUM-ION BATTERY SEAL

(60) Provisional application No. 60/346,031, filed on Nov. 9, 2001.

# Alkaline earth aluminoborate glasses have the requisite properties for lithium battery seals

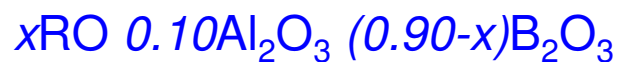


- Range of CTEs for variety of pin materials
- Relatively low sealing temperatures (<800° C)
- CABAL glasses are used in Na-vapor lamps
- Resist attack by lithium
  - kinetic stability (Li reduces  $B_2O_3$  to boride)
  - >20 year projected battery lifetime

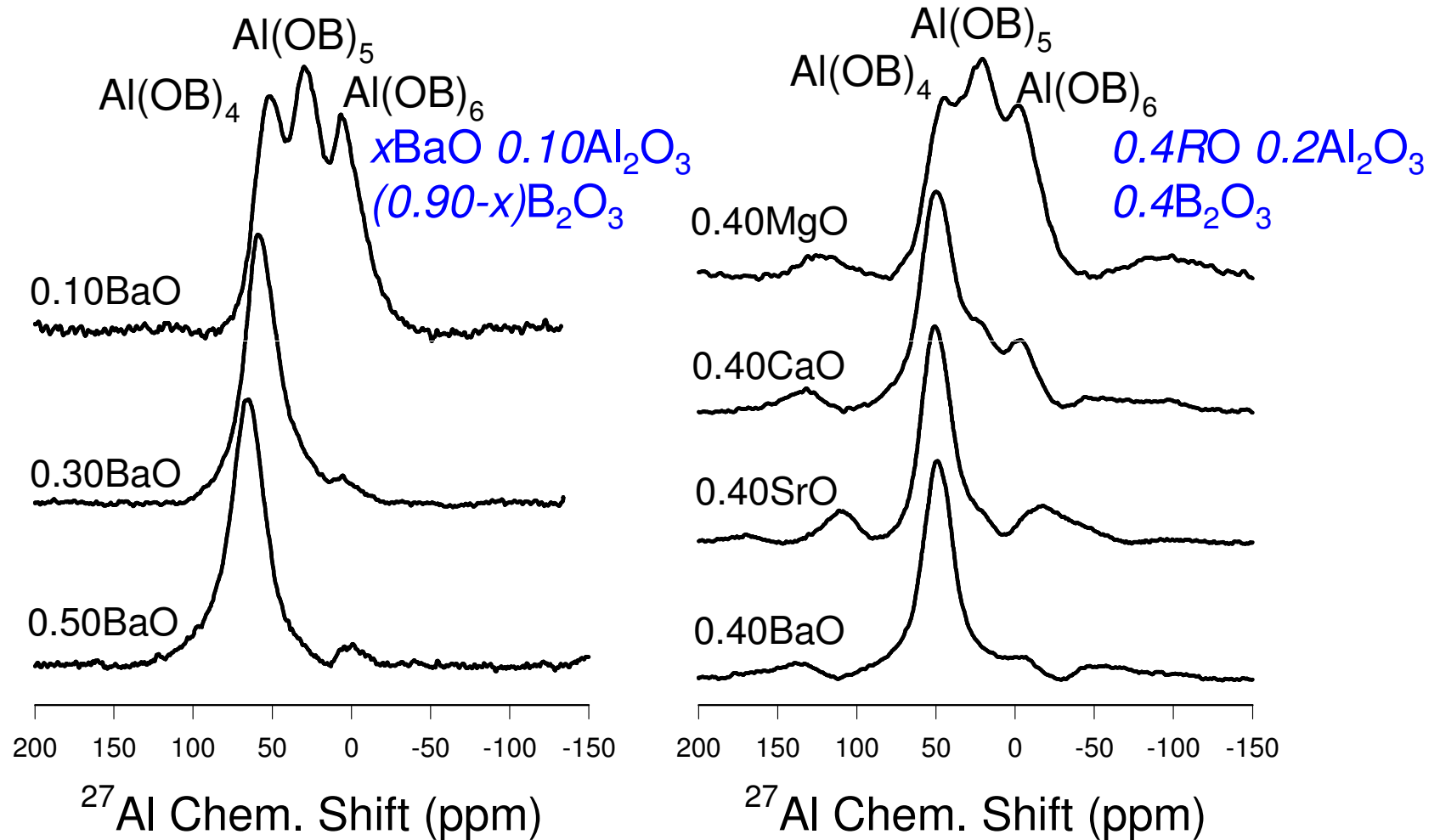
How does structure affect useful properties?



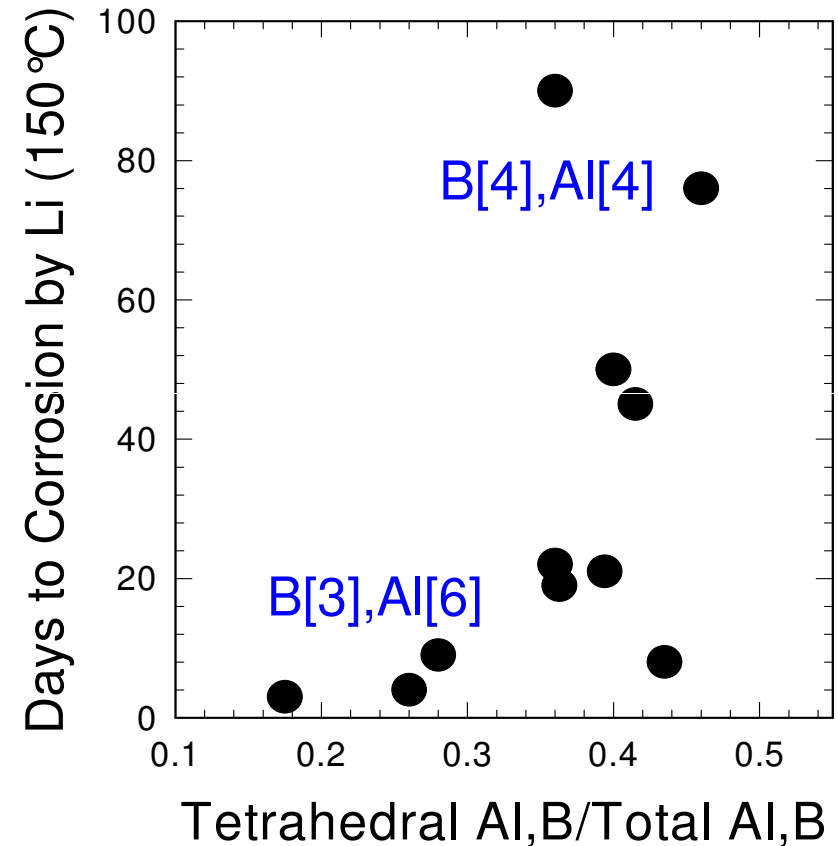
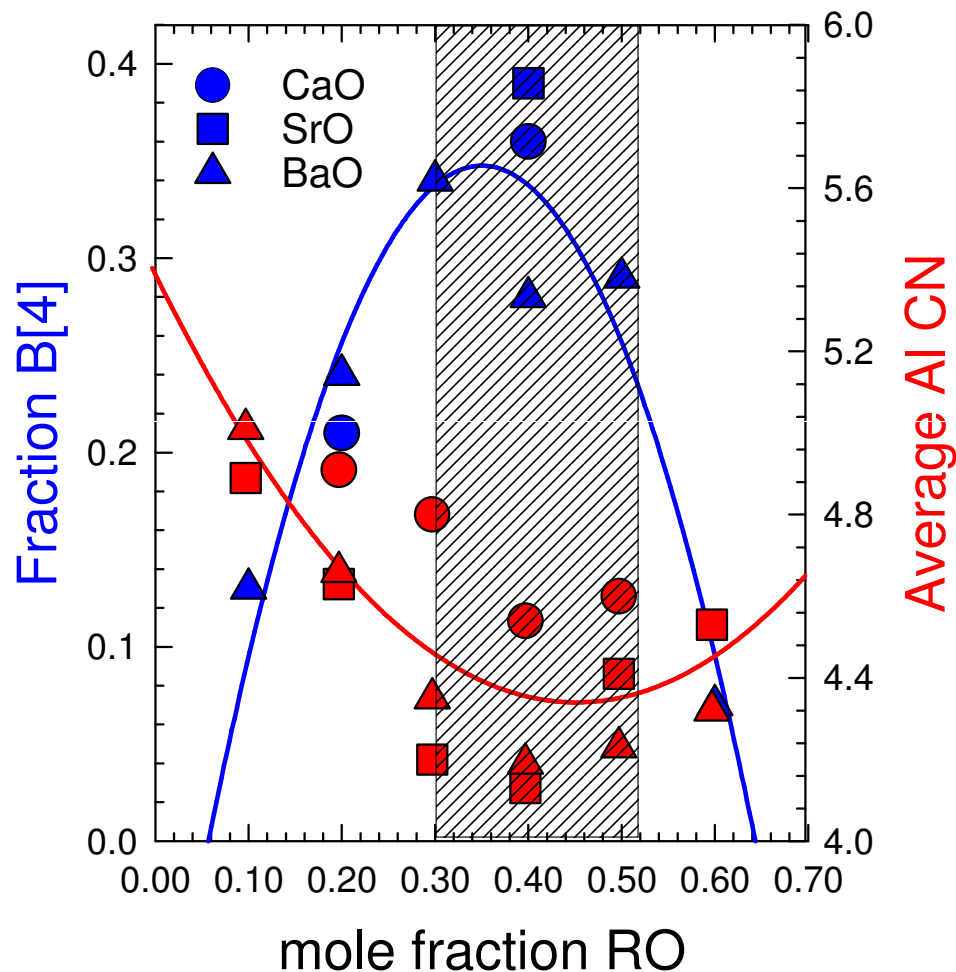
# Glass properties depend structure



# Alumina coordination also depends on composition



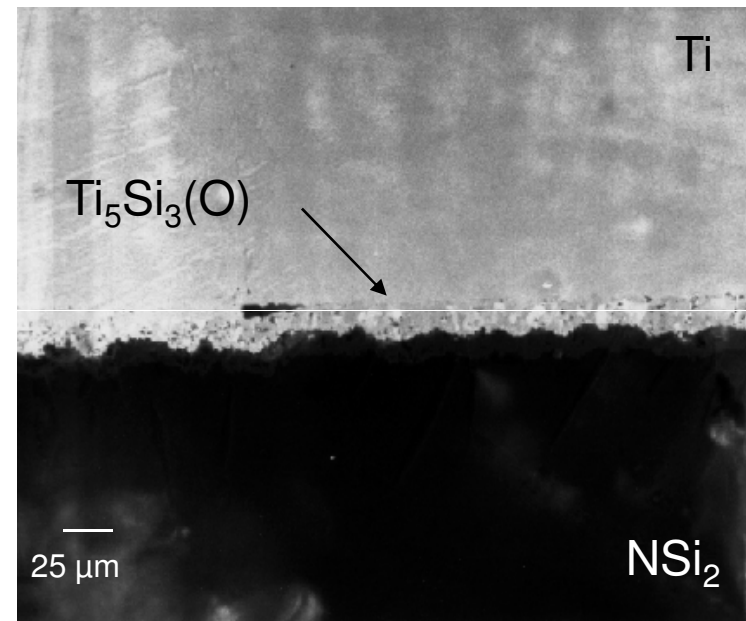
# The most durable glasses have tetrahedral networks



Aqueous durability exhibits similar structural dependencies

## Spin-Off Development: Titanium Sealing Glasses

- Titanium alloys have a variety of useful properties
  - High strength-to-weight ratio
  - Superior corrosion resistance
  - Reasonable weldability
- Potential Sealing Applications:
  - Satellite connectors, actuators
  - Implanted biomedical components (pacemakers, insulin pumps, etc.)
  - Biocompatible coatings on prosthetic alloys

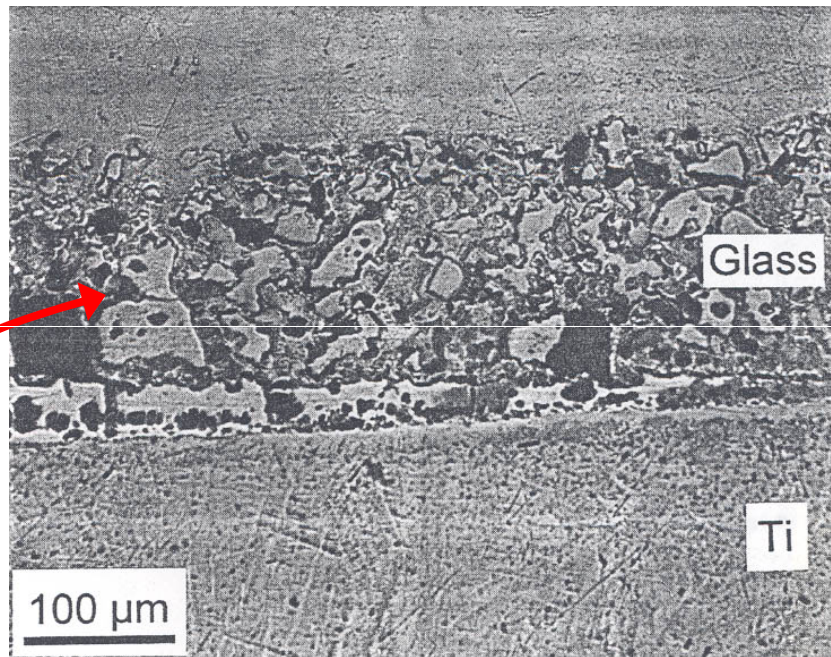


**Limitation: Reliable, commercial hermetic sealing technology**

- conventional silicate sealing glasses are reduced by titanium
  - silicide formation leads to weak glass/Ti interfaces

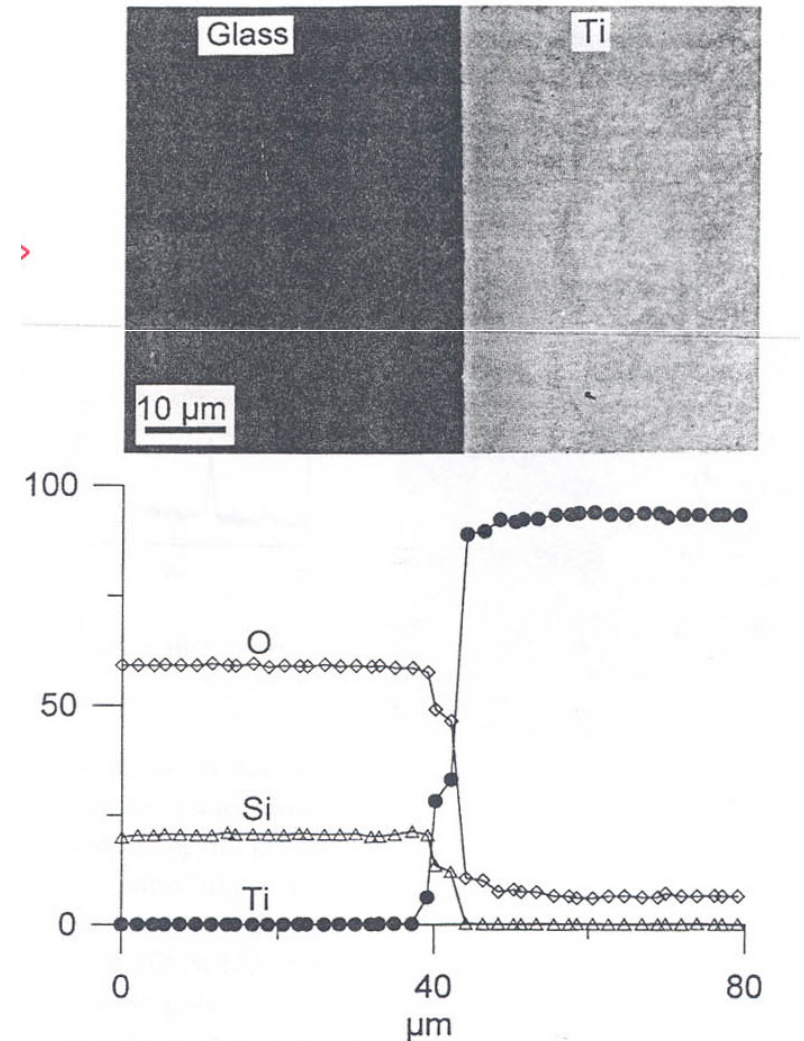
# Silicate bio-glass coatings for titanium require very short processing times

800°C/1 minute: no deleterious reactions between silicate glass and Ti.



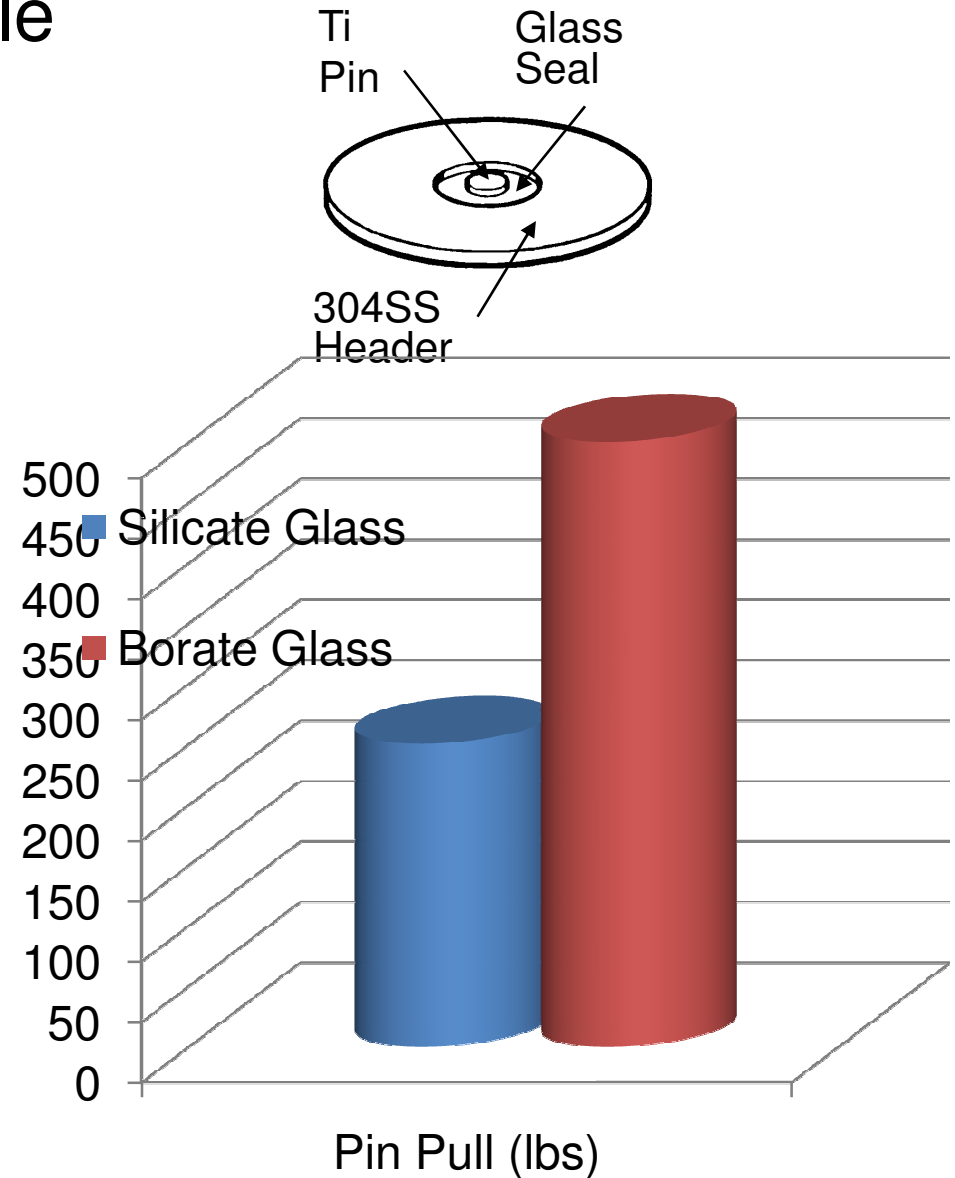
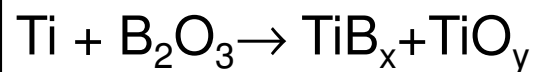
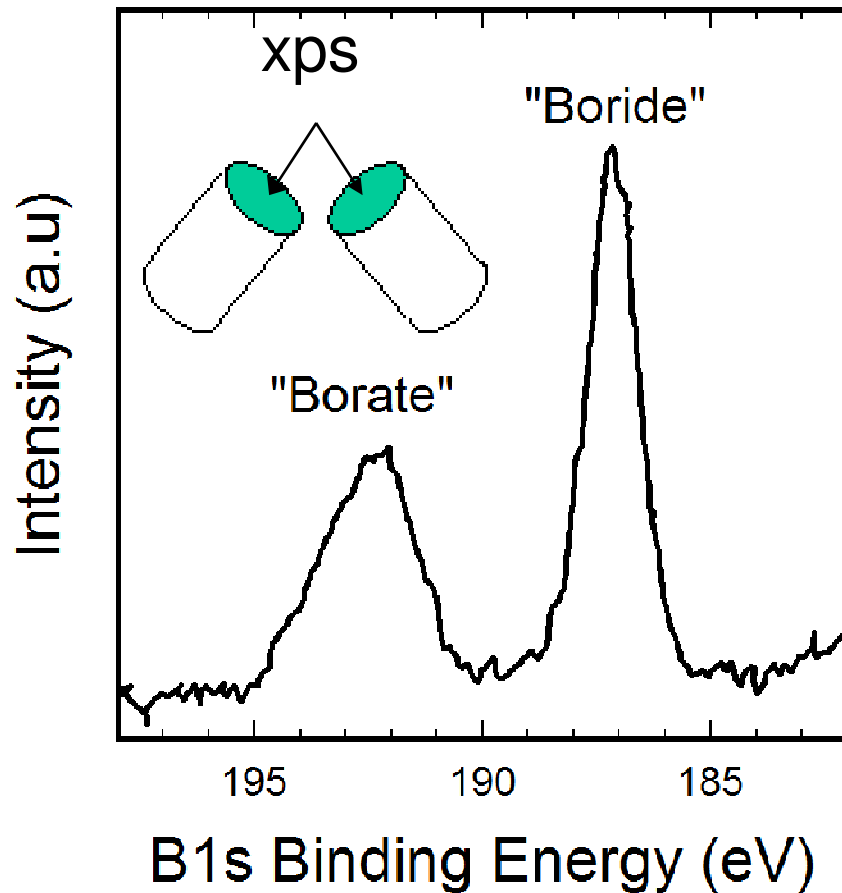
900°C/1 minute: excessive interfacial reactivity between Bioglass and Ti.

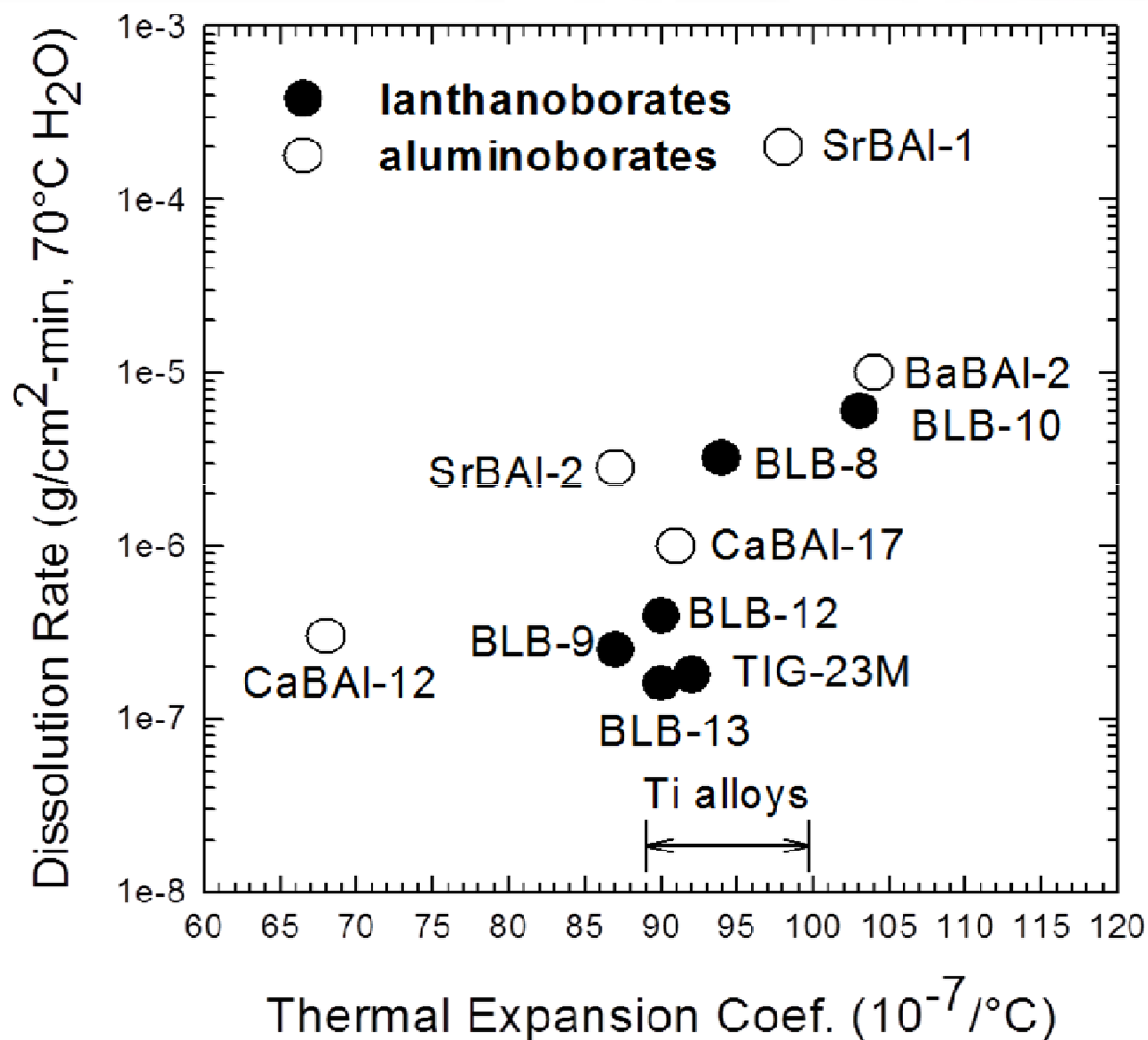
Pazo et al (1998)



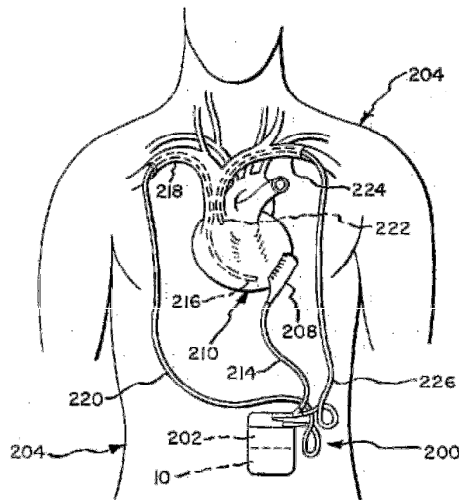


# Borate glasses are compatible with titanium alloys

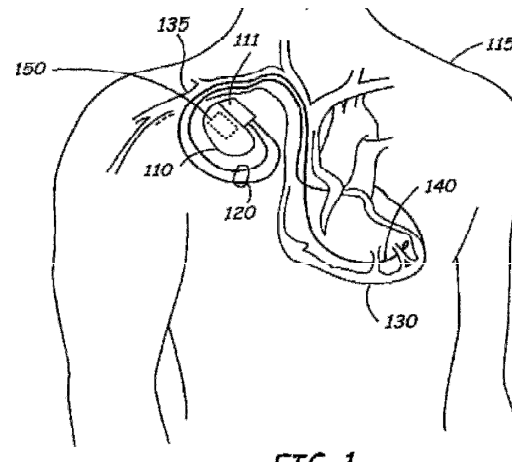




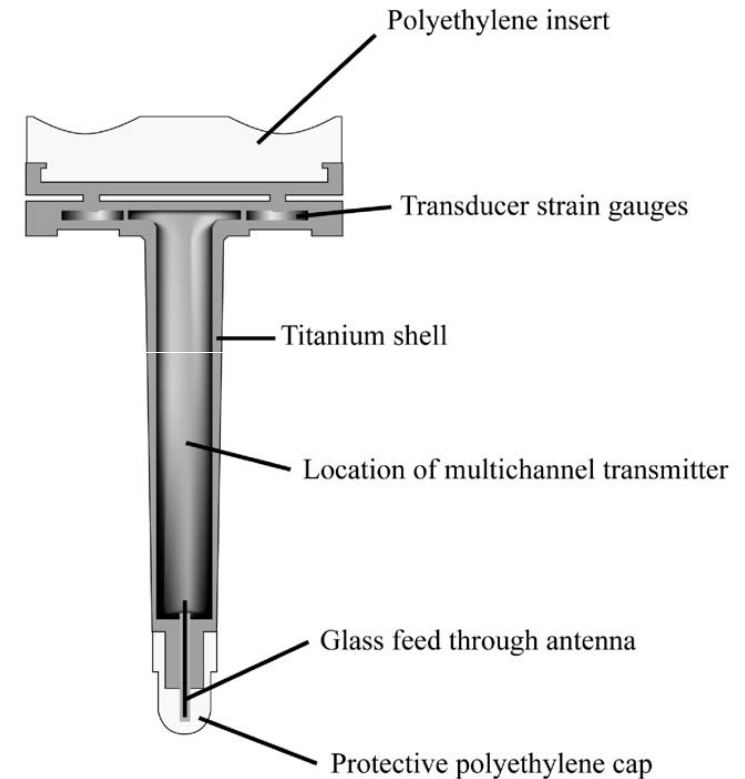
# Borate glasses are now being used in a variety of titanium biomedical applications



Pacemakers and defibrillators



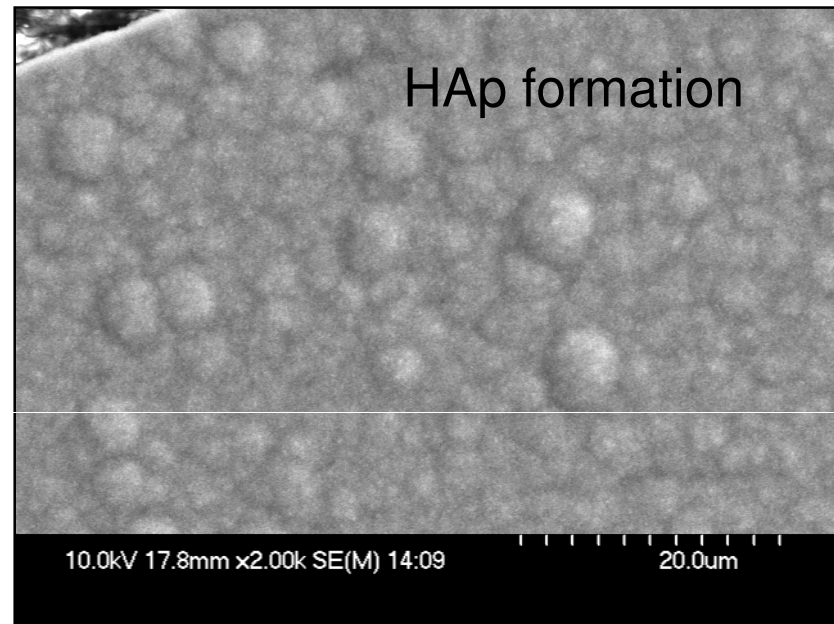
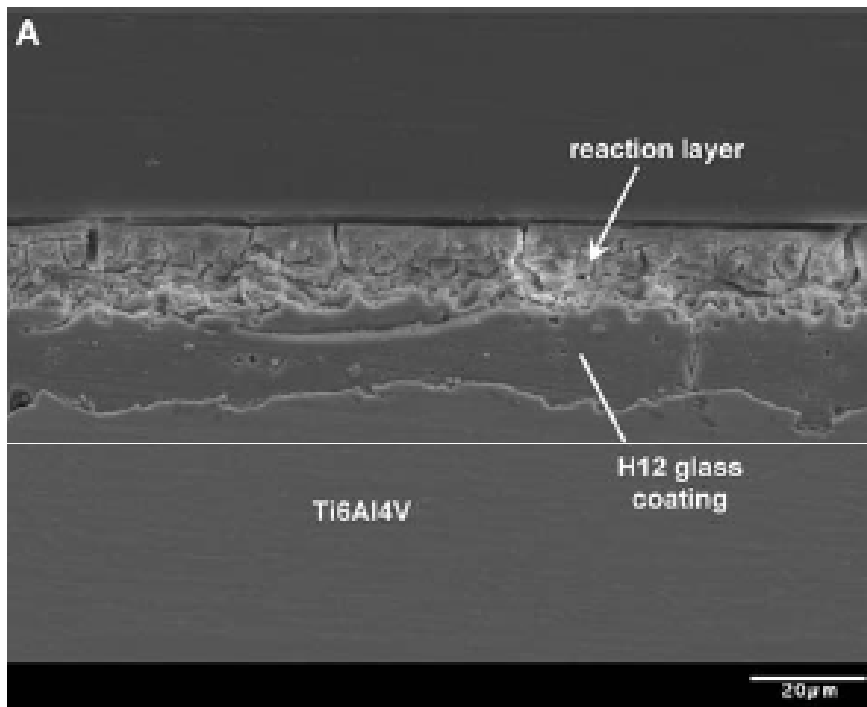
Insulin pumps



Orthopedic pressure sensors

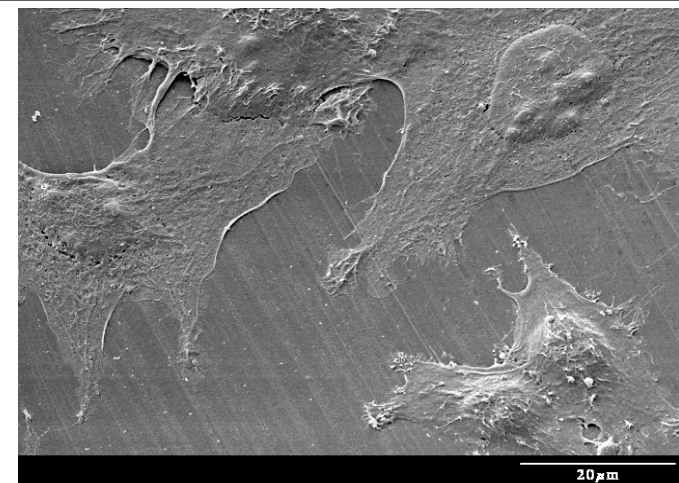


## Bioactive borate glass coatings have been developed for titanium



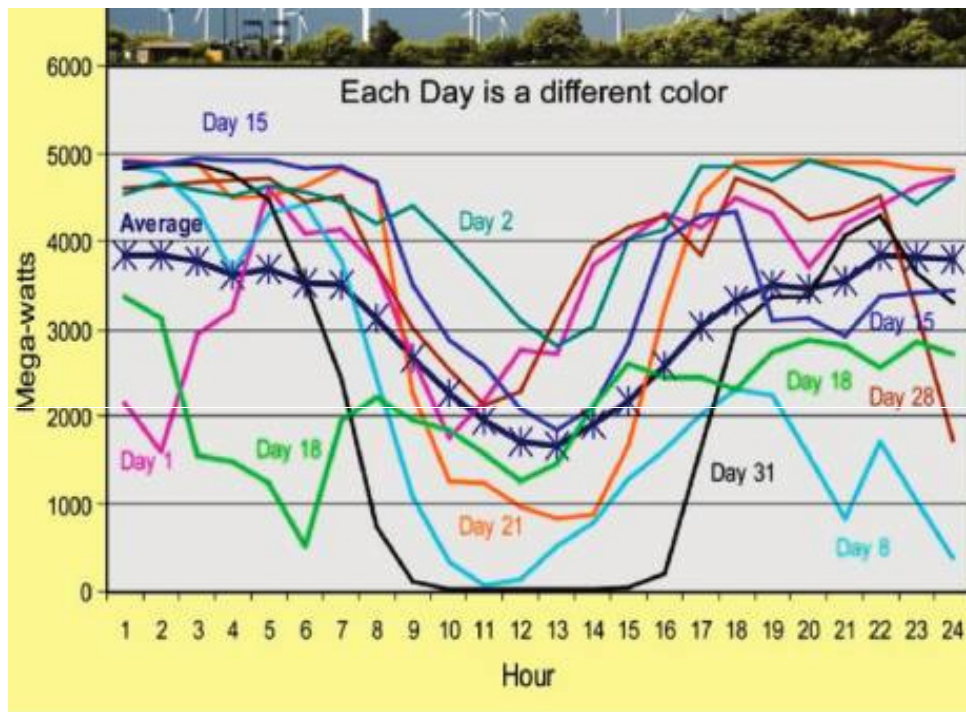
L. Peddi, RK Brow and RF Brown, J. Mater. Sci. Mater Med (2008) 19, 3145

Saos-2 cell compatibility

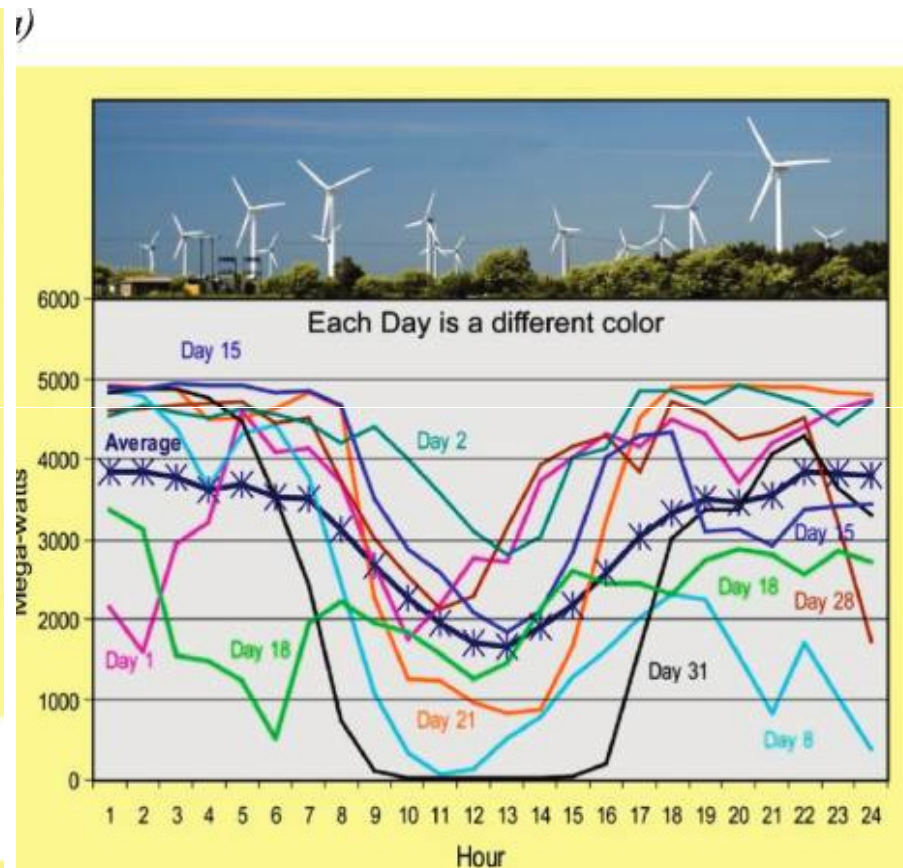


# Alkali Thermal Battery Seals

## Electrochemical energy storage for the green energy grid



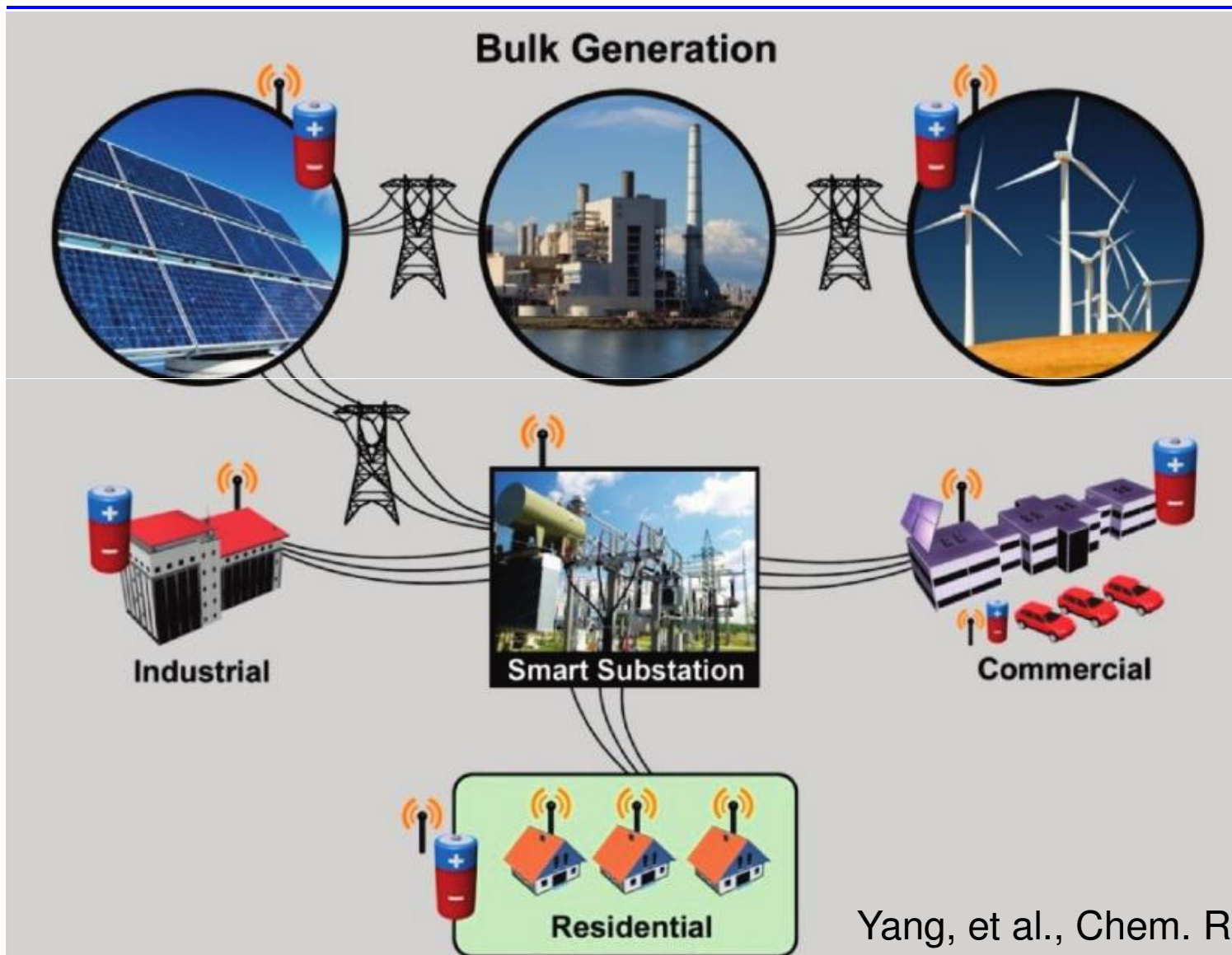
b)



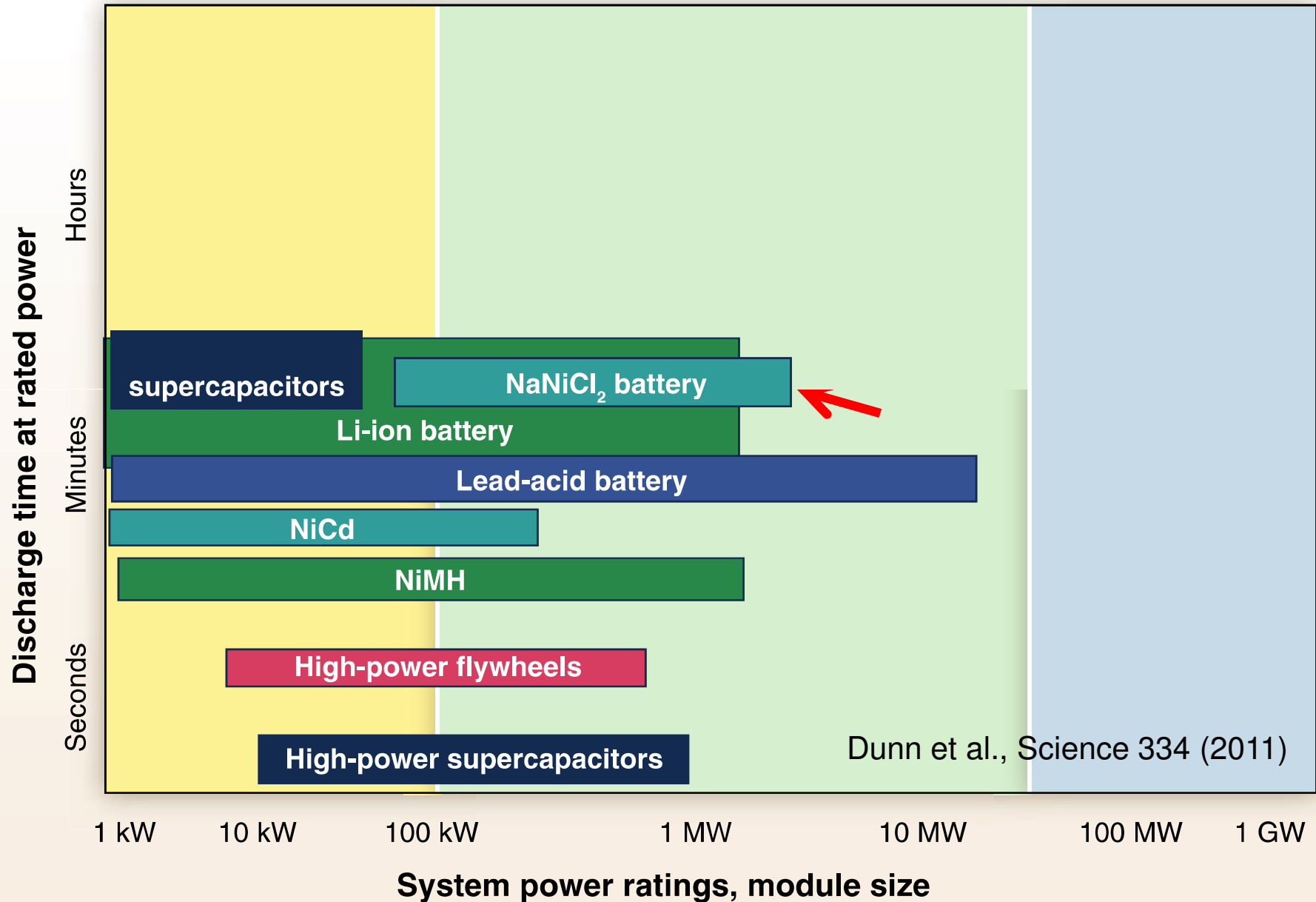
Yang, et al., Chem. Rev. (2011)



# Advanced batteries will be part of the green energy grid



Yang, et al., Chem. Rev. (2011)



## Cell

requirements

$\beta$ - $\text{Al}_2\text{O}_3$

compatibility

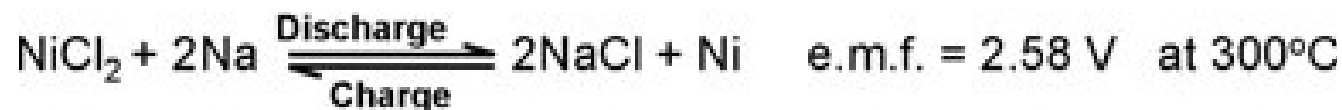
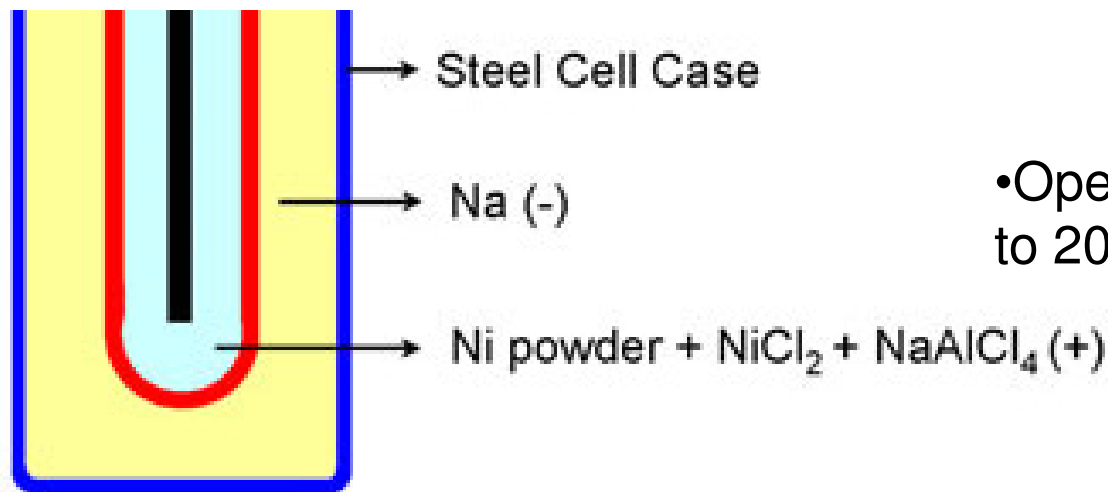
in, gaseous Na and

es (electrolyte)

'poisoning' ions for

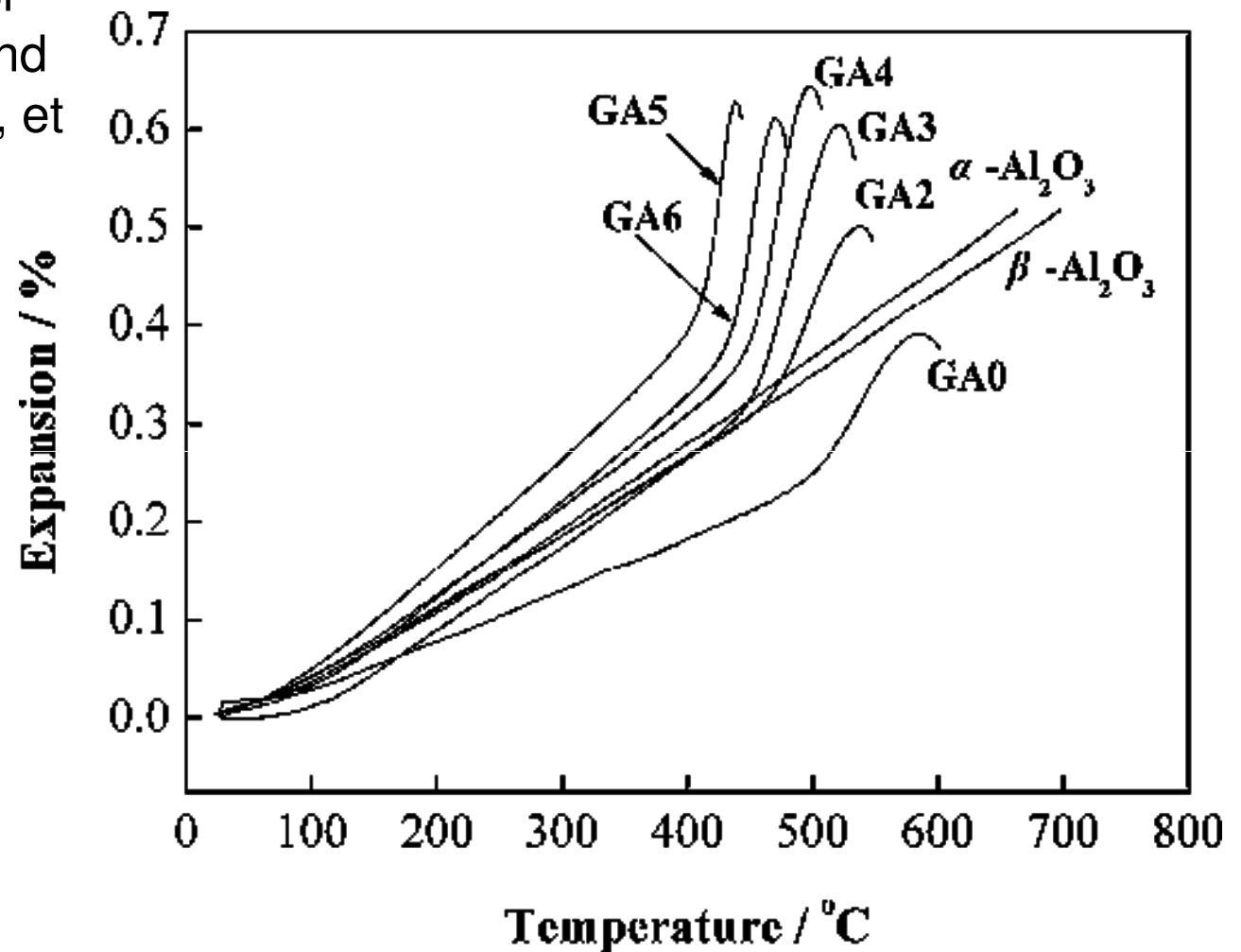
$\beta$ - $\text{Al}_2\text{O}_3$  (sealing  
reactions)

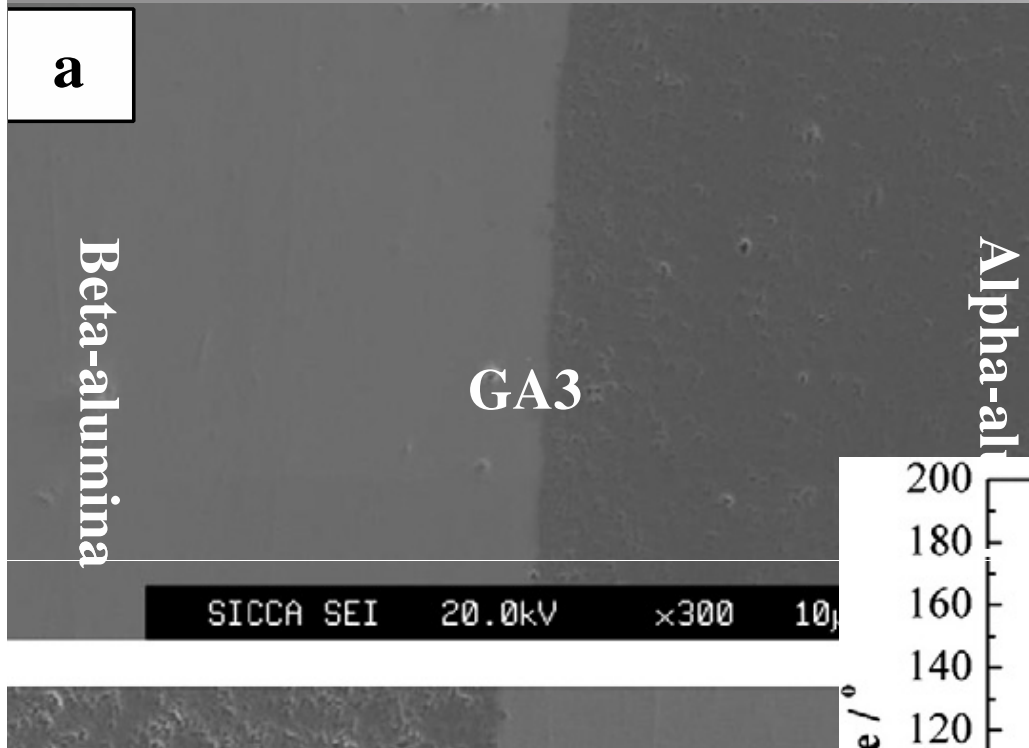
• Operate at 300-400° C for up  
to 20 years



Example: Low alkali Bi-borosilicate glasses and glass-ceramics (Song, et al., JNCS (2011))

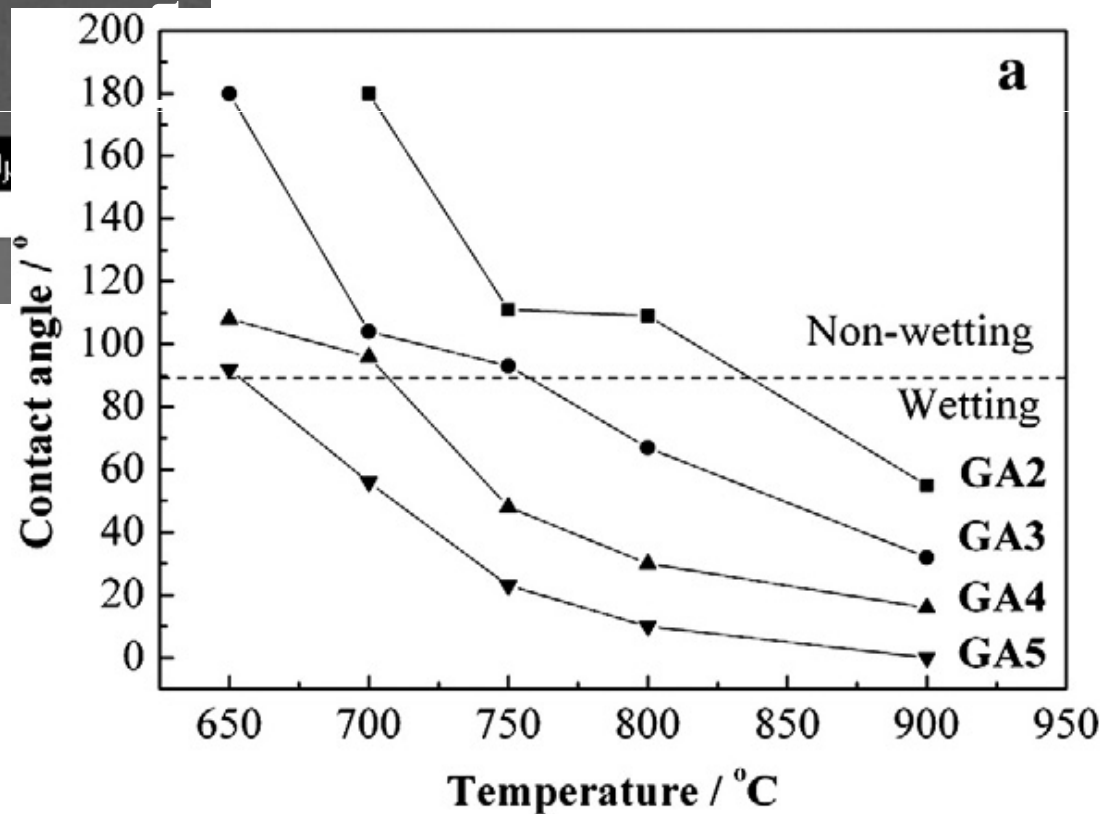
0-62  $\text{Bi}_2\text{O}_3$   
replacing  $\text{SiO}_2$





Example: Low alkali Bi-borosilicate glasses and glass-ceramics (Song, et al., JNCS (2011))

Wetting behavior on  $\beta$ -Al<sub>2</sub>O<sub>3</sub>





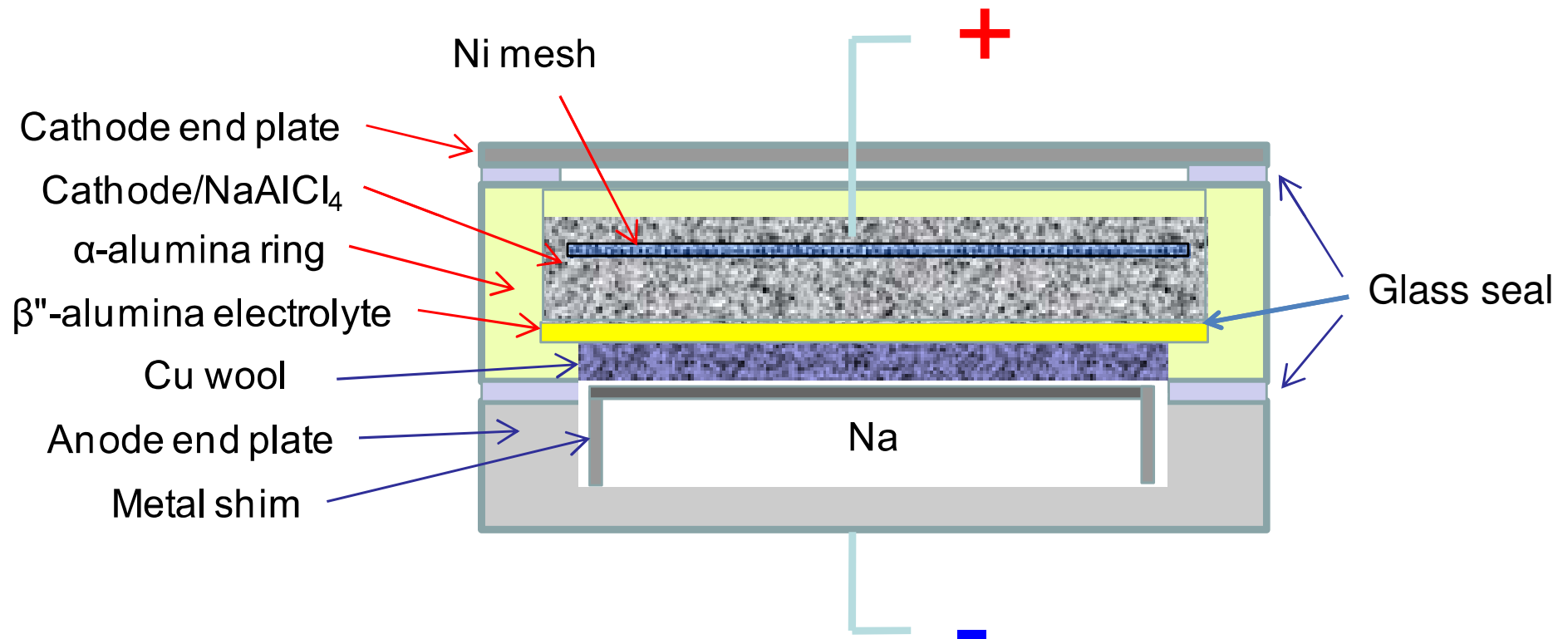
## Still, there is an opportunity for new sealing materials

“Major obstacles to demonstrating long-life liquid metal batteries center on ... the engineering of robust, high temperature, insulating seals.”- Kim et al., Liquid Metal Batteries: Past, Present, and Future, Chemical Reviews (2013)

“Chemically stable sealants” are one of the outstanding materials problems remaining for Na/S batteries- Cheng et al. Advanced Materials (2011)

## New designs face more complex sealing challenges

Planar Na/NiCl<sub>2</sub> stack for load-leveling applications: same  $\alpha$ -to- $\beta$  alumina seal, but added alumina-steel seal



Lu et al., High Power Planar Sodium-Nickel Chloride Battery, ECS Trans. 28(22) 7 (2010)

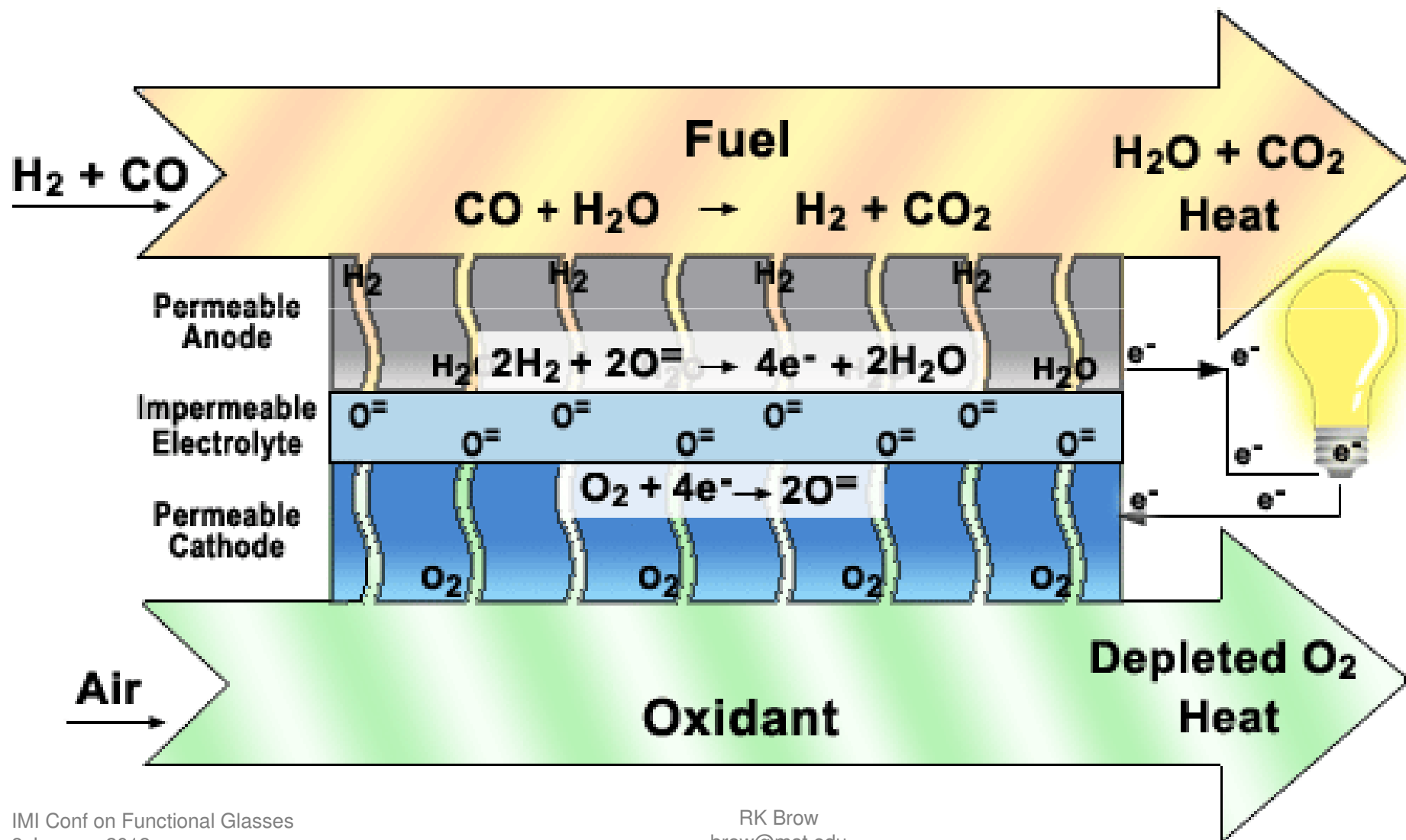
# Solid Oxide Fuel Cells

From I. Donald, et al., J Mater Sci  
(2011) 46:1975–2000



**Fig. 6** SOFCs. Experimental unit. Julich Research Centre 13.3 kW

## Solid Oxide Fuel Cell



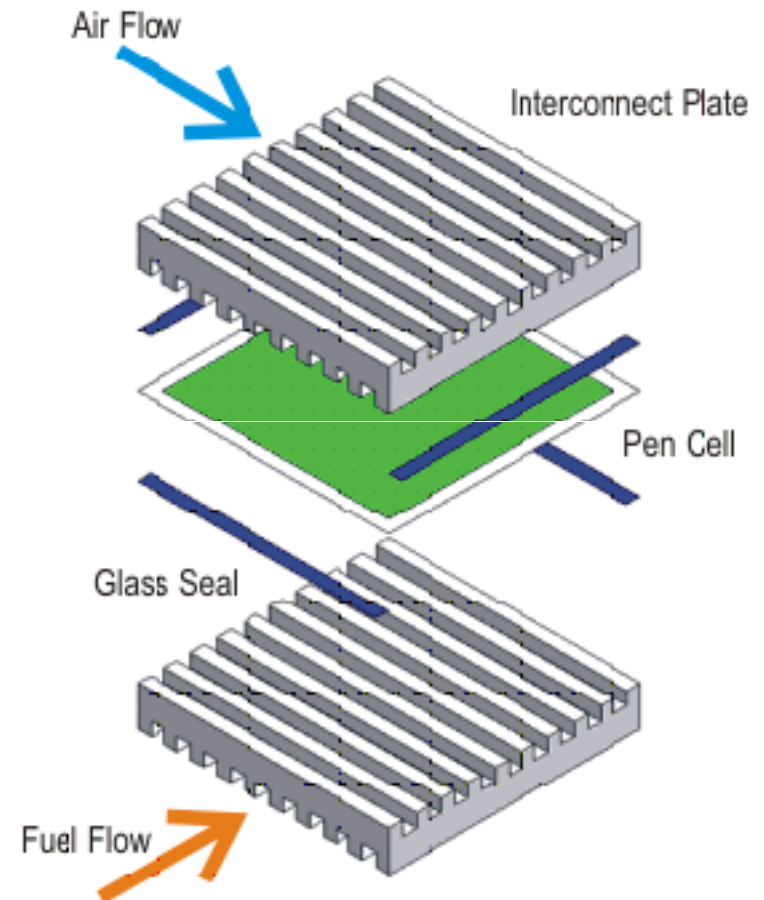
## Designing glasses for SOFC seals is a significant challenge

### Function:

- Prevent mixing of fuel/oxidant within stack
- Prevent leaking of fuel/oxidant from stack
- Electrically isolate cells in stack
- Provide mechanical bonding of components

### Challenges:

- Thermal expansion matches to a variety of materials
- Relatively high operational temperatures ( $>700^{\circ}\text{C}$ )
  - Long lifetimes ( $>10000'$  s hrs)
  - Maintain stability over range of  $P_{\text{O}_2}$ ,  $P_{\text{H}_2\text{O}}$
- Relatively low sealing temperatures ( $<900^{\circ}\text{C}$ )
  - Avoid altering other SOFC materials



For some designs, glass-ceramics may be suitable, others may require viscous seals



There have been a number of recent reviews of SOFC sealing glasses

J Mater Sci (2007) 42:3465–3476  
DOI 10.1007/s10853-006-0409-9

J. Mat. Sci. (2007)

**A review of sealing technologies applicable to solid oxide electrolysis cells**

Journal of Power Sources 147 (2005) 46–57

J. Power Sources, (2005)

Review

Sealants for solid oxide fuel cells

Jeffrey W. Fergus\*

Contents lists available at [ScienceDirect](#)

Materials Science and Engineering R

journal homepage: [www.elsevier.com/locate/mser](http://www.elsevier.com/locate/mser)

Glass-based seals for solid oxide fuel and electrolyzer cells – A review

M.K. Mahapatra, K. Lu\*

Mat Sci Eng B (2010)

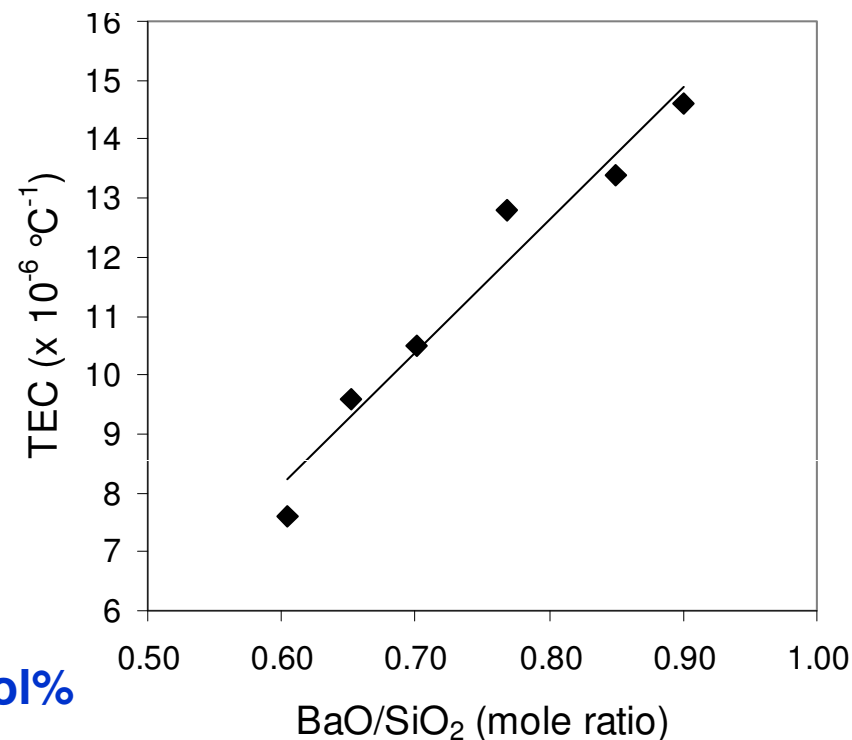
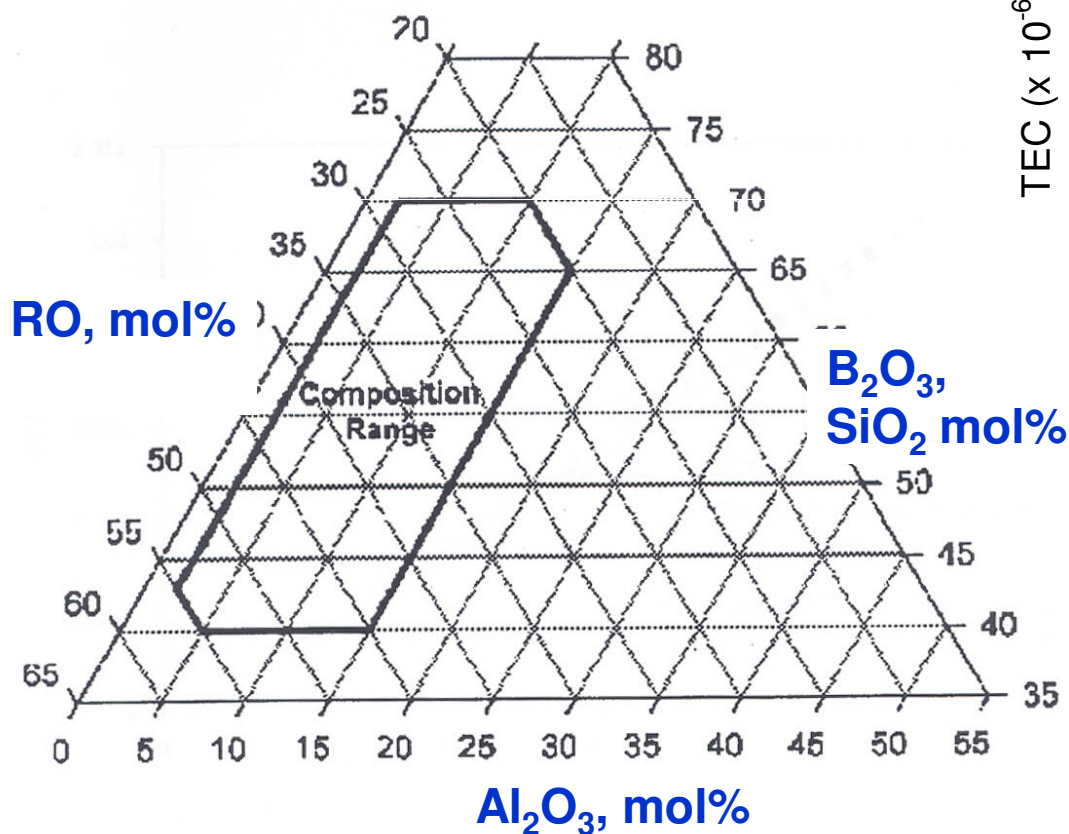
**The State-of-the-Art in Sealing Technology for Solid Oxide Fuel Cells**

K. Scott Weil

JOM, August 2006

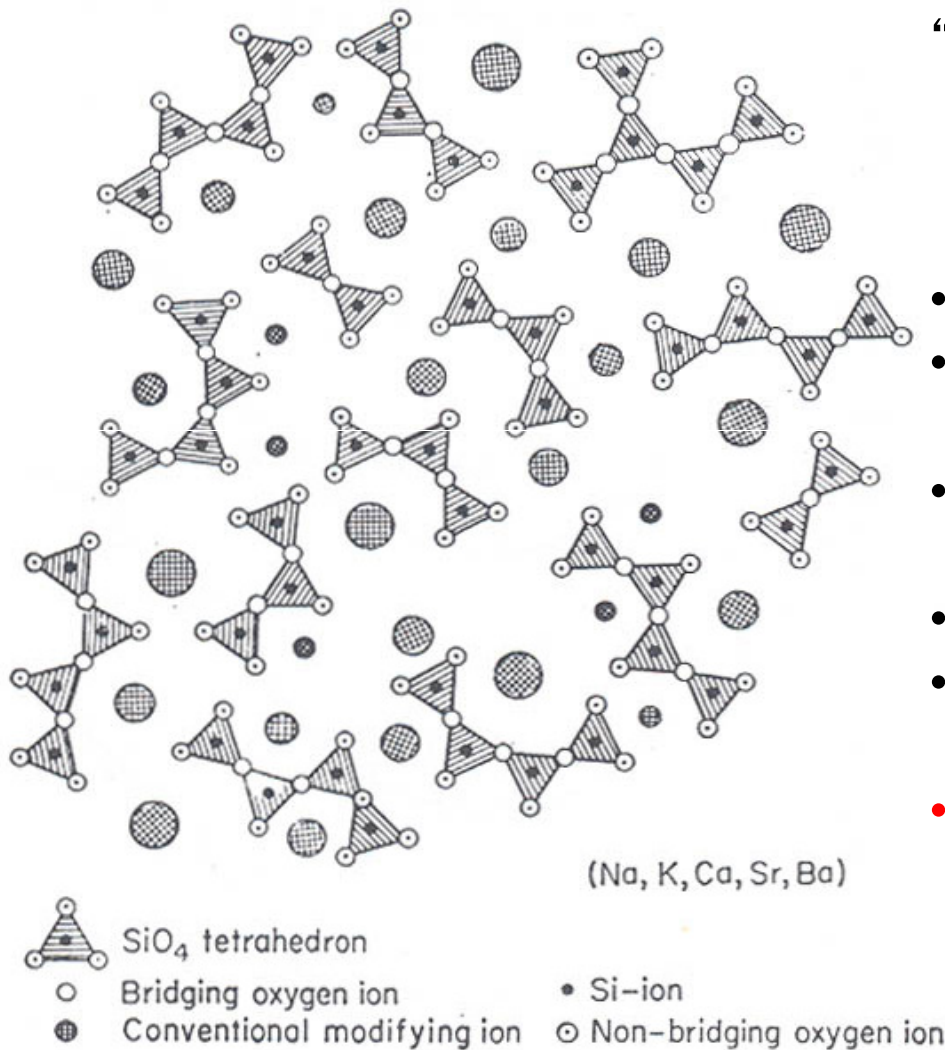
# Ba-silicate glass-ceramics have shown promise

Meinhardt, et al., USP 6,532,769  
Mar. 18, 2003



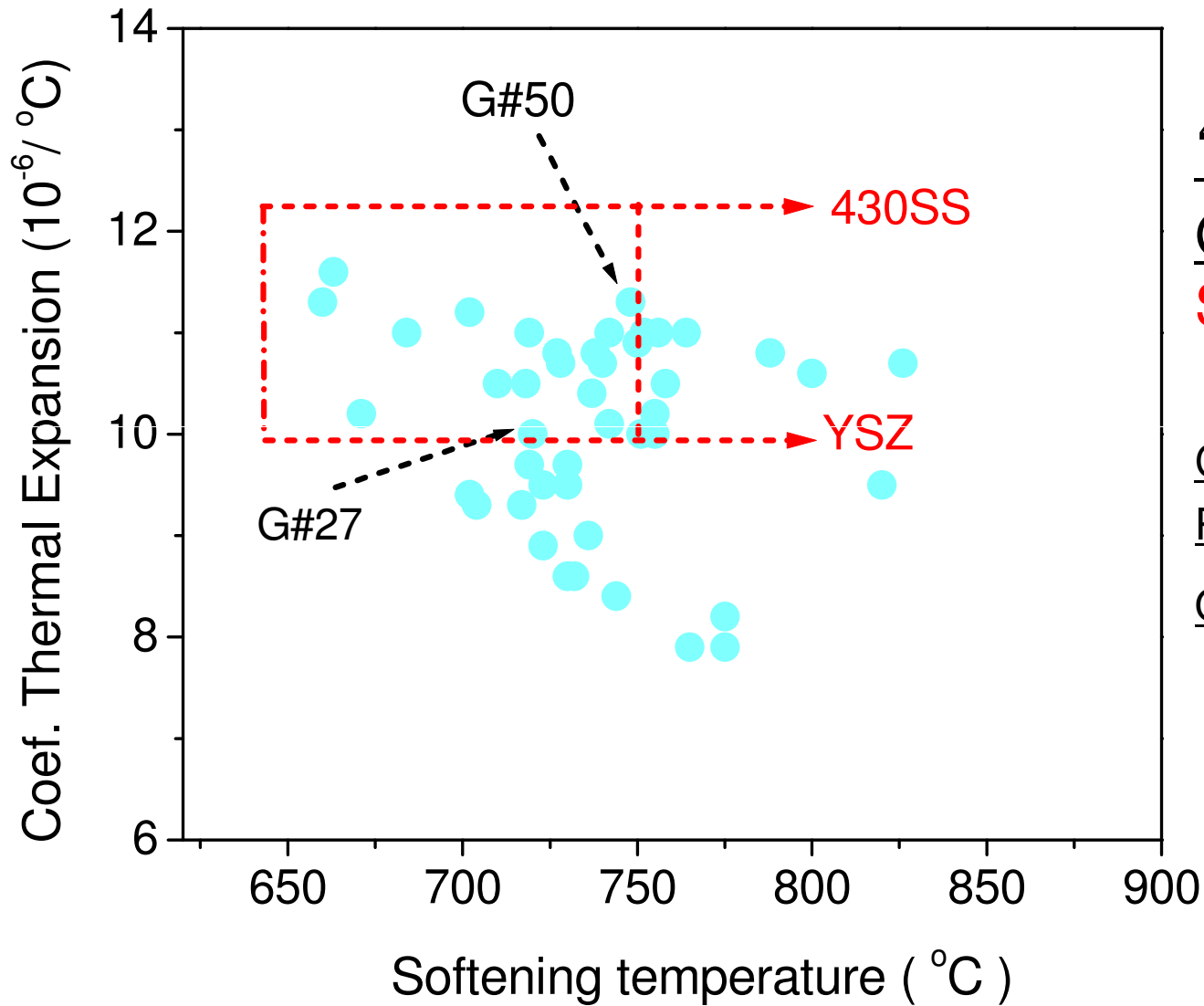
Sealed, crystallized to form high CTE Ba-silicate & Ba-alumino-silicate phases;  
e.g., BaO·2SiO<sub>2</sub>, 2BaO·3SiO<sub>2</sub>

# Candidate sealing glasses have 'invert' structures



**“Invert Glasses”**: discontinuous silicate anions tied-together through modifying cations.

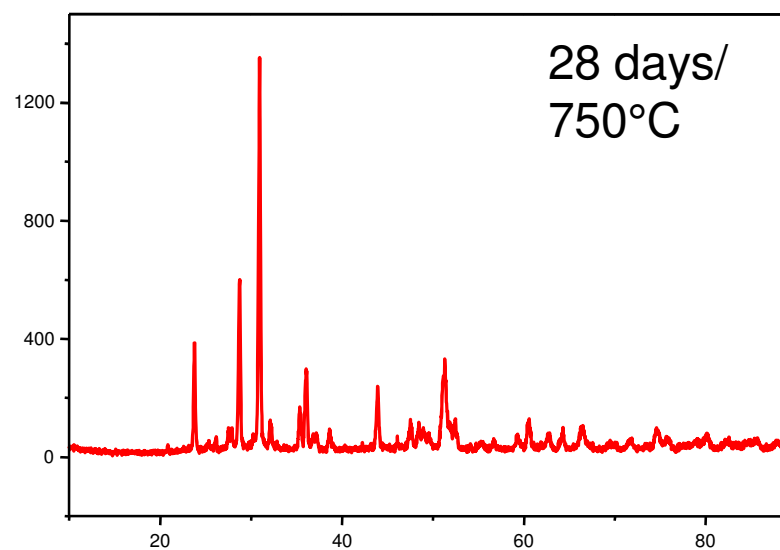
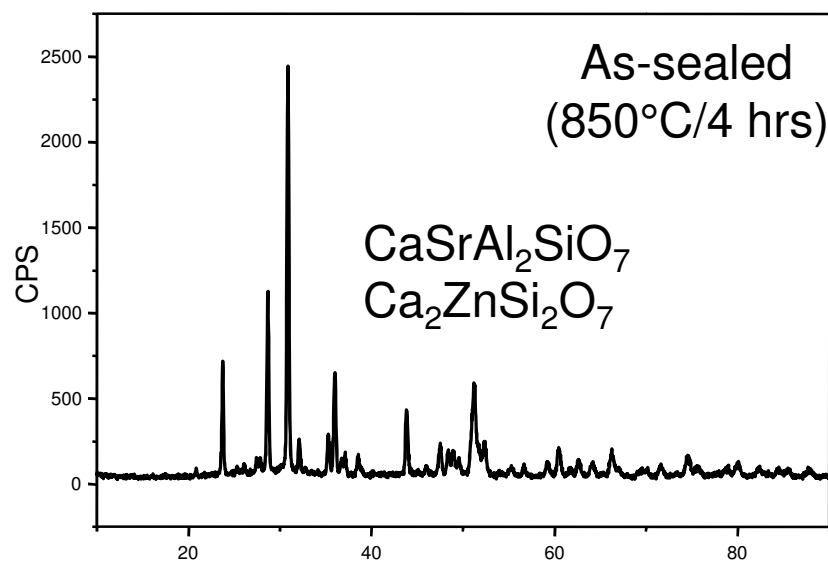
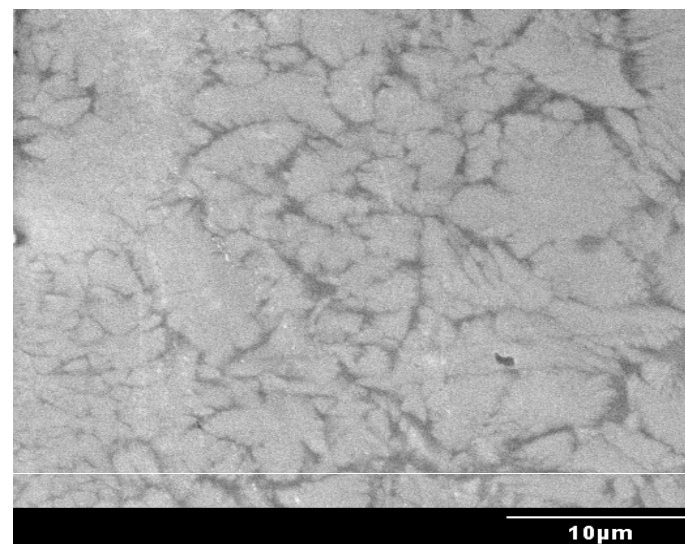
- Greater CTE's
- More fragile viscosity behavior
  - ‘shorter’ glasses
- More ‘basic’ reaction chemistries
- Metasilicates (chains):  $[\text{O}]/[\text{Si}] \sim 3.0$
- Polysilicates (short chains):  $[\text{O}]/[\text{Si}] > 3.0$
- **Greater CTEs from polysilicate crystalline phases**



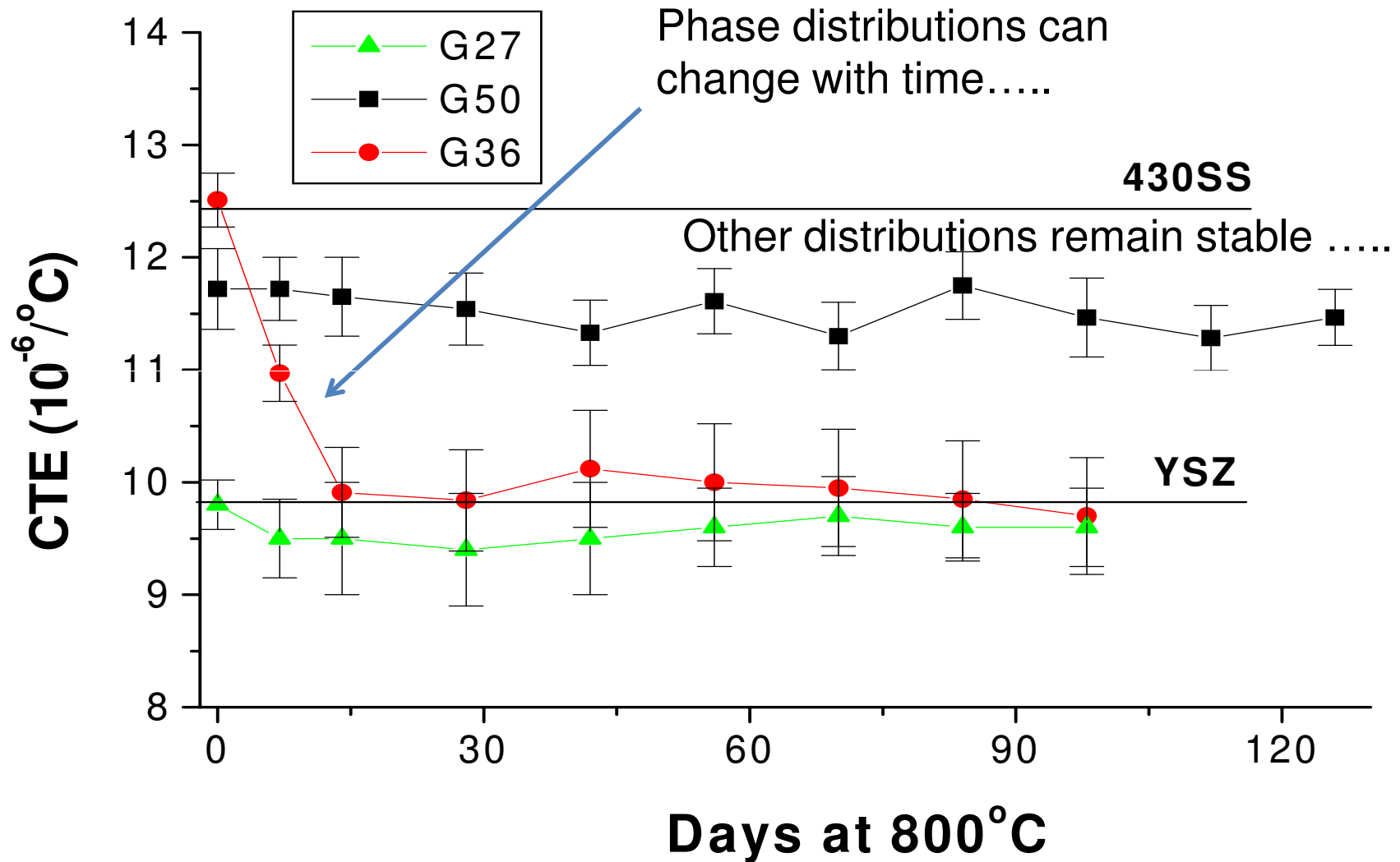
“Invert” silicate:  
Glasses with  
 $\text{SiO}_2 < 45 \text{ mole\%}$

Compositions based on:  
Pyrosilicate and  
Orthosilicate phases

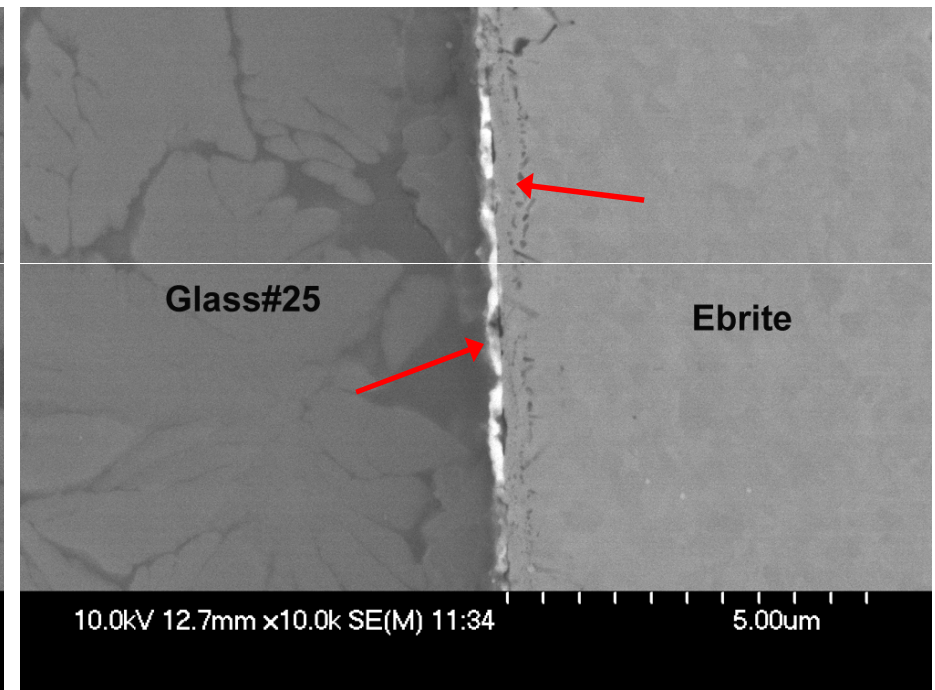
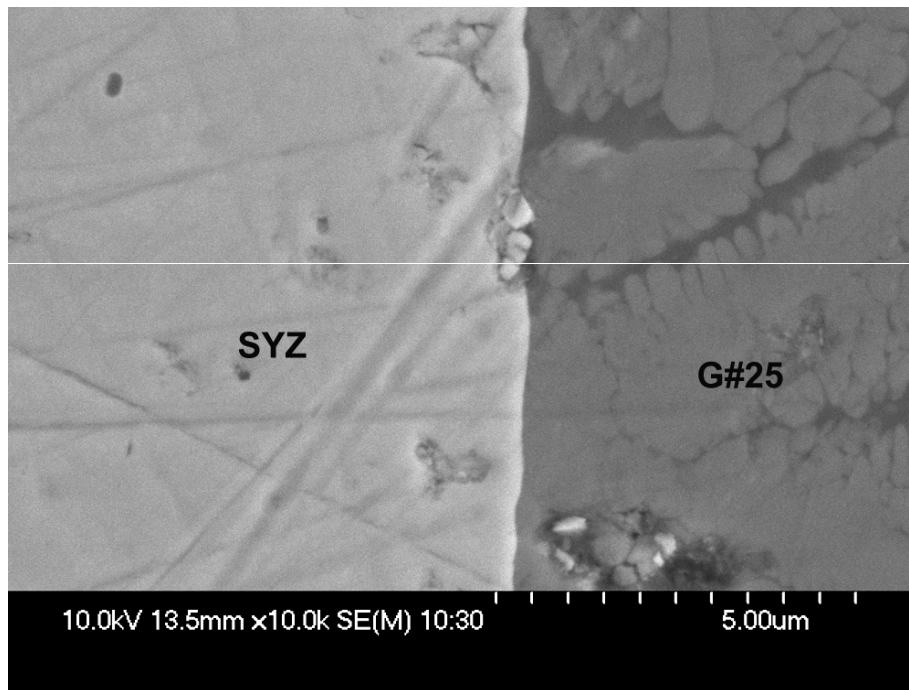
- **Pyrosilicates**
  - $\text{CaSrAl}_2\text{SiO}_7$ ,  $\text{Ca}_2\text{ZnSi}_2\text{O}_7$
- **Orthosilicates**
  - $\text{Sr}_2\text{SiO}_4$ ,  $\text{Zn}_2\text{SiO}_4$
- The crystalline phases appear to be thermally stable.







# Thermo-mechanically robust seals can be made to SOFC component materials

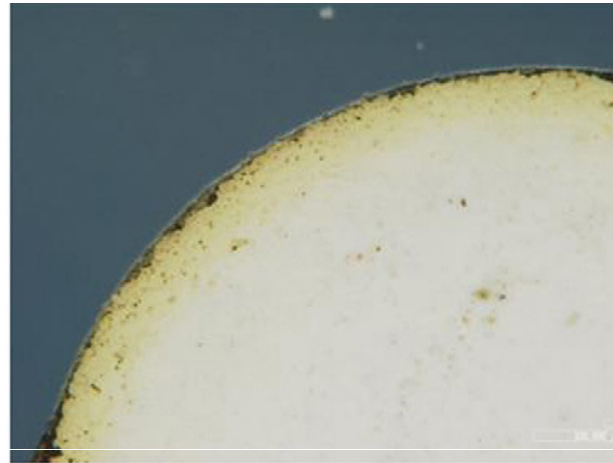


750° C/two weeks in air

One potential problem is deleterious reactions with chromia



As sealed

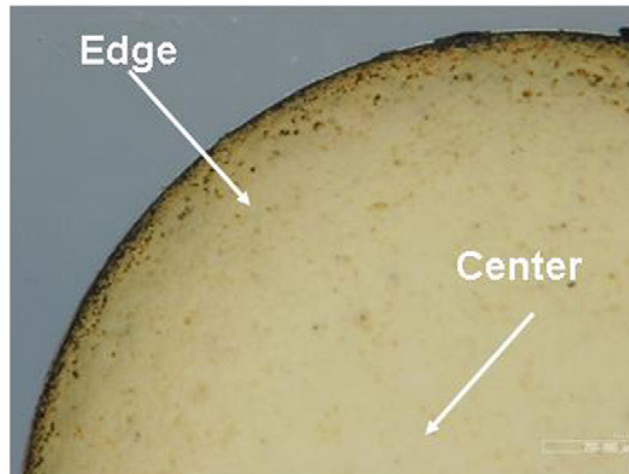


800°C for 1 we

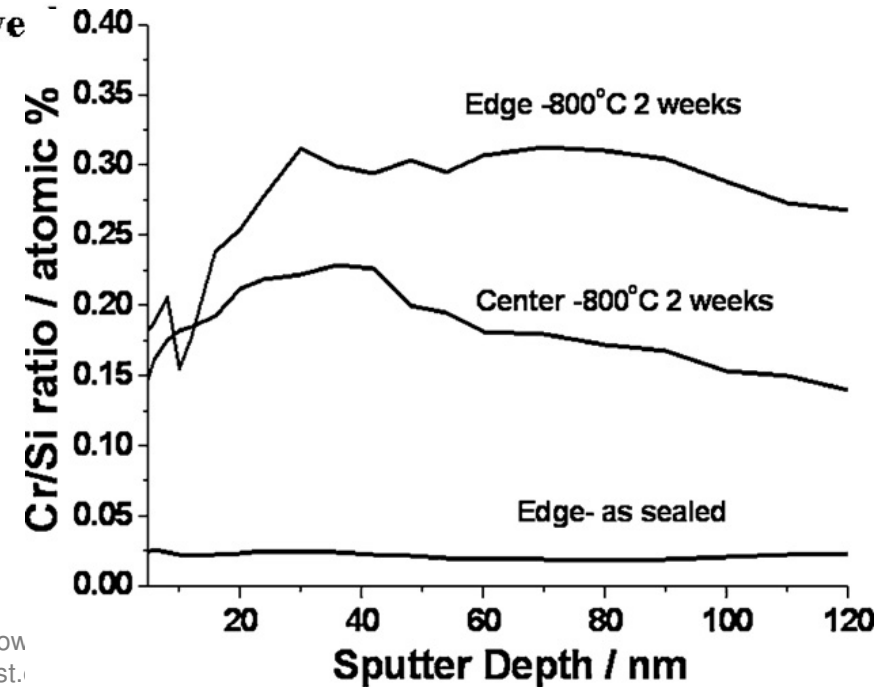
CTE mismatches occur at the glass-metal interface:

BaCrO<sub>4</sub>: 18 ppm/K

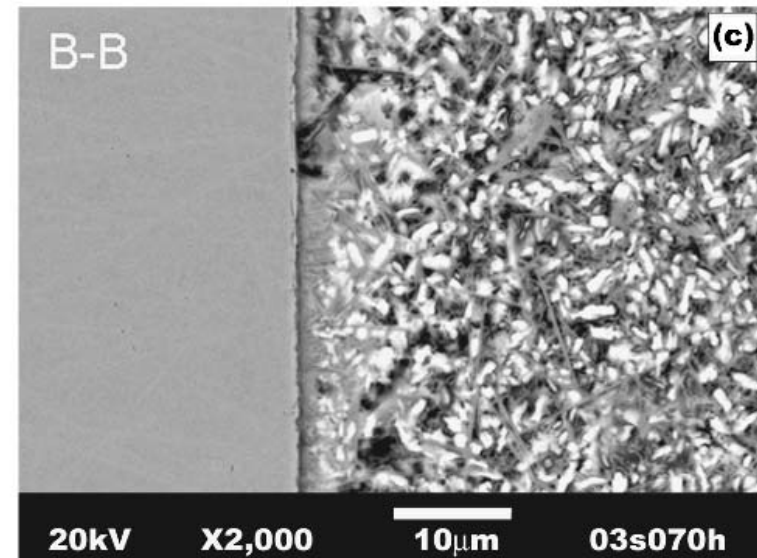
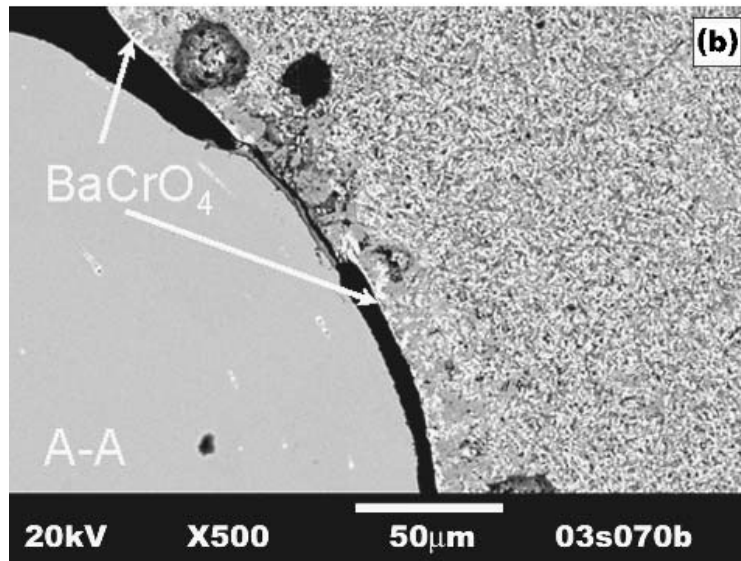
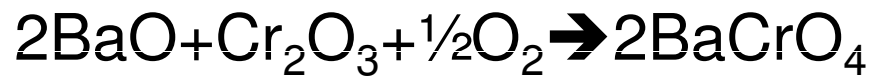
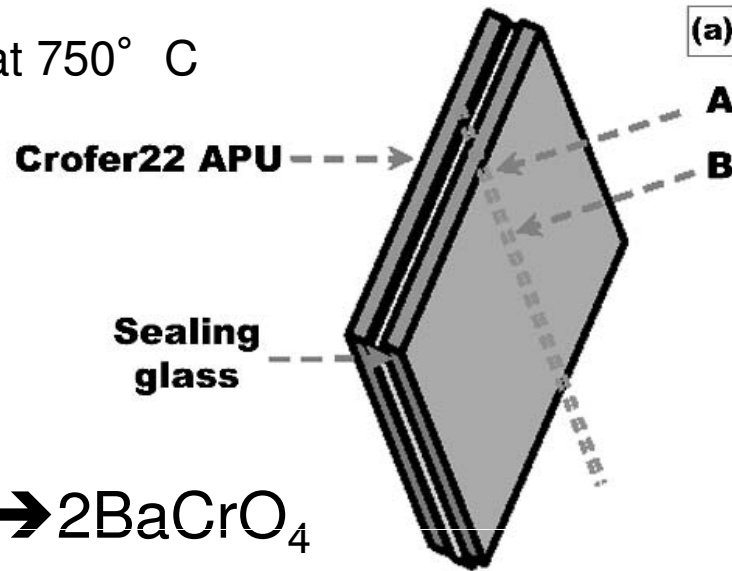
Steel/Glass: 12ppm/K



800°C for 2 weeks



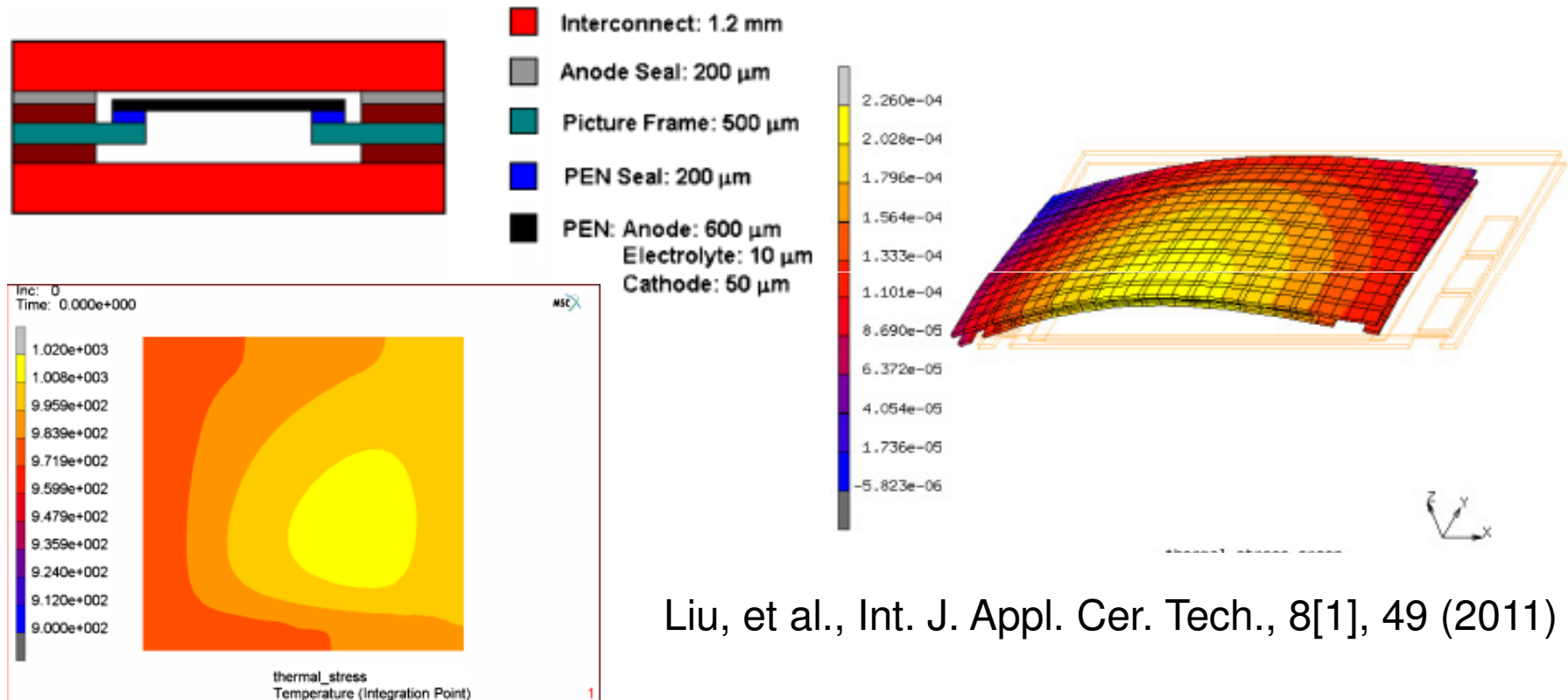
G18/Crofer after 1 week at 750° C



Yang et al., JMEPEG 13, 327 (2004)



A second problem with 'rigid' glass-ceramic seals involves the thermal stresses associated with slight CTE mismatches



Liu, et al., Int. J. Appl. Cer. Tech., 8[1], 49 (2011)

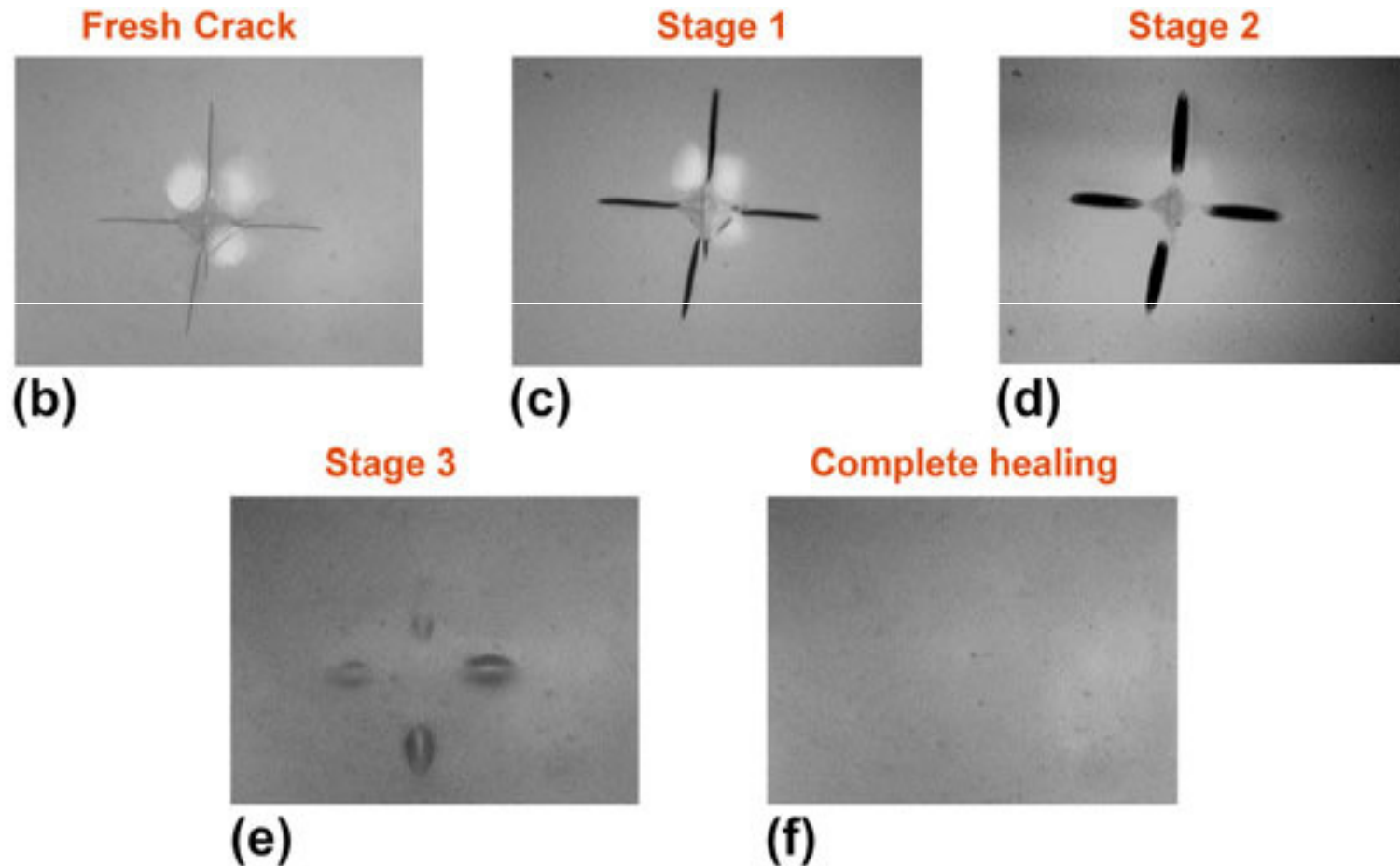
One solution may be to use a 'viscous' seal that will 're-heal' on heating



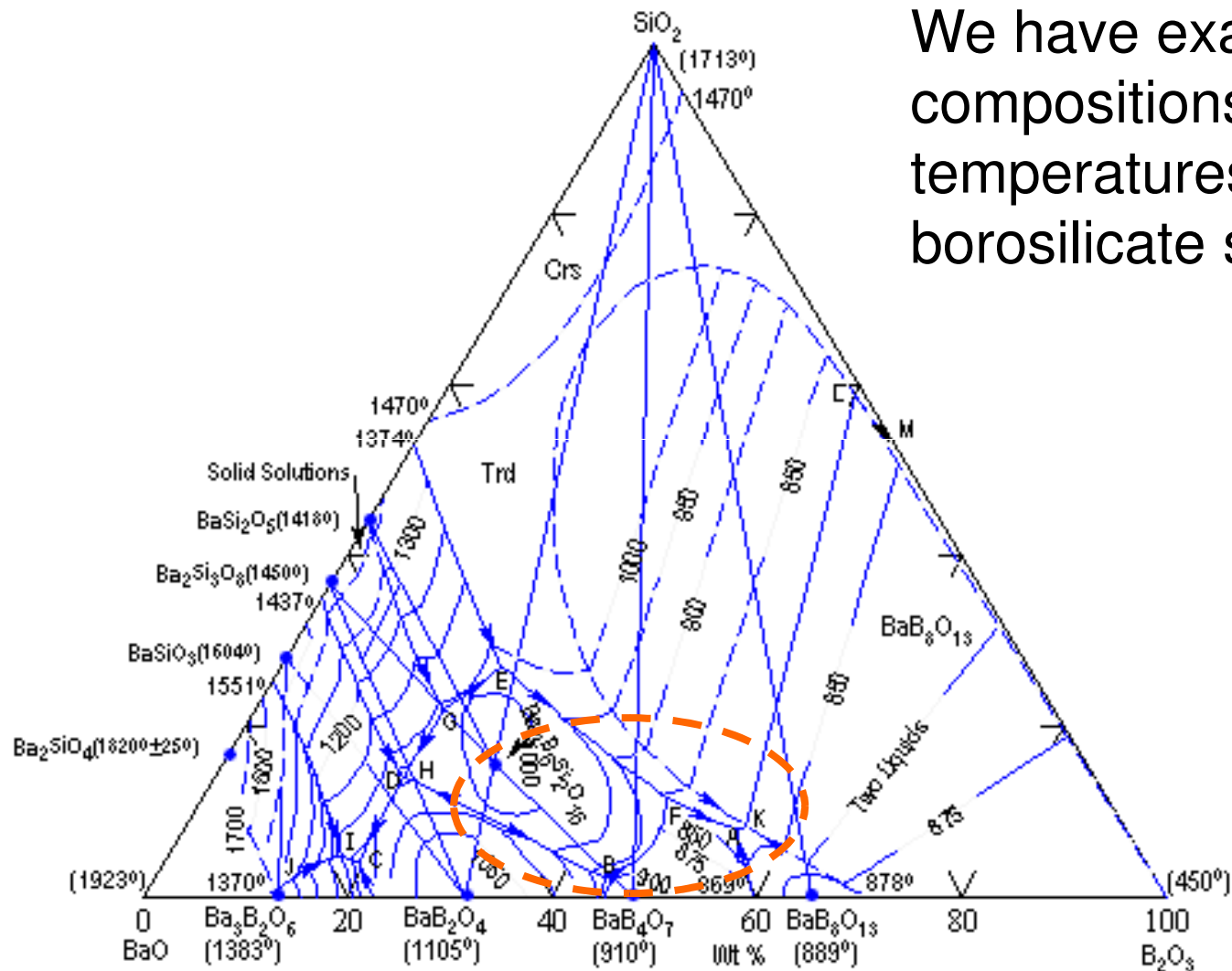
## Self-repairable glass seals for solid oxide fuel cells

Raj N. Singh<sup>a)</sup>

School of Materials Science and Engineering, Oklahoma State University, Tulsa, Oklahoma 74106-0700

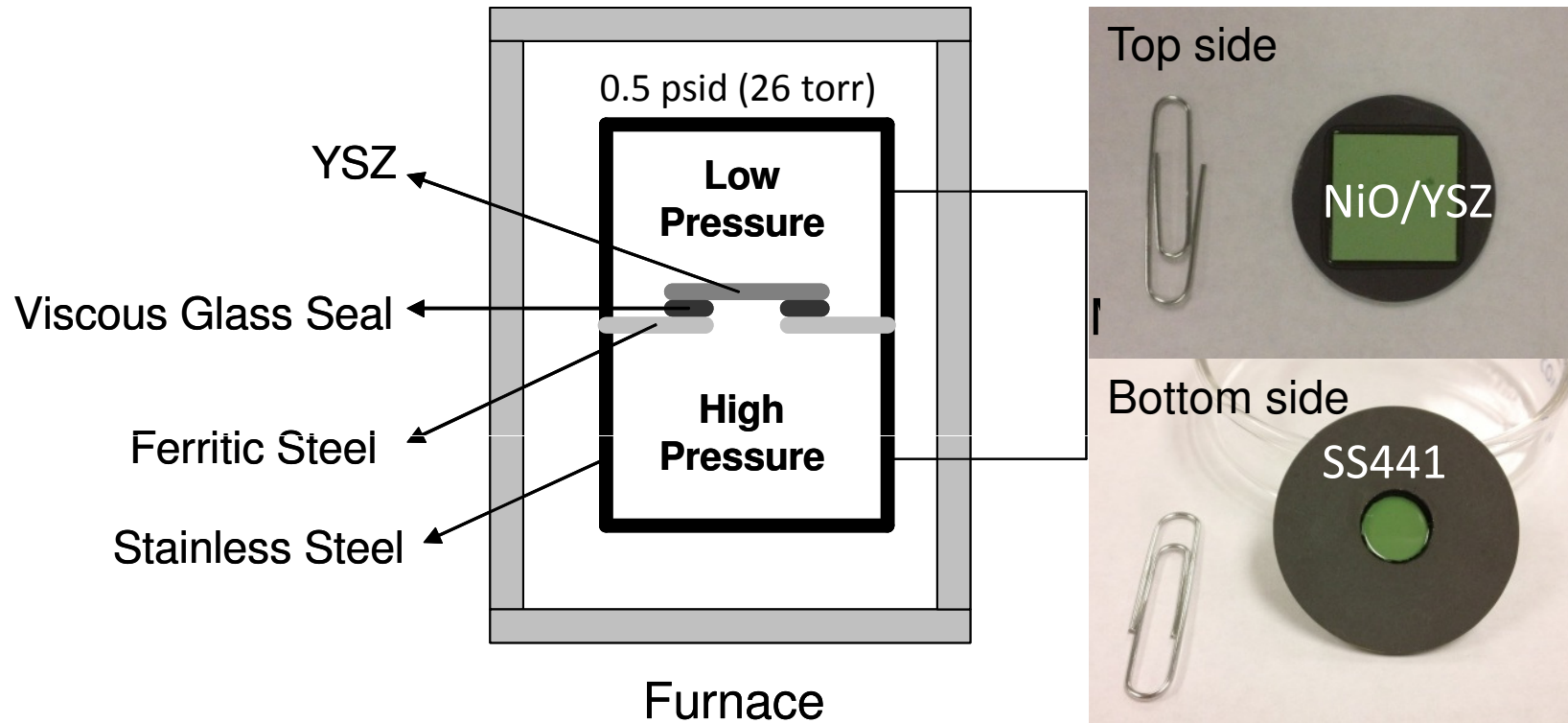


Singh, J. Mater. Res., 27[15] 2055 (2012)



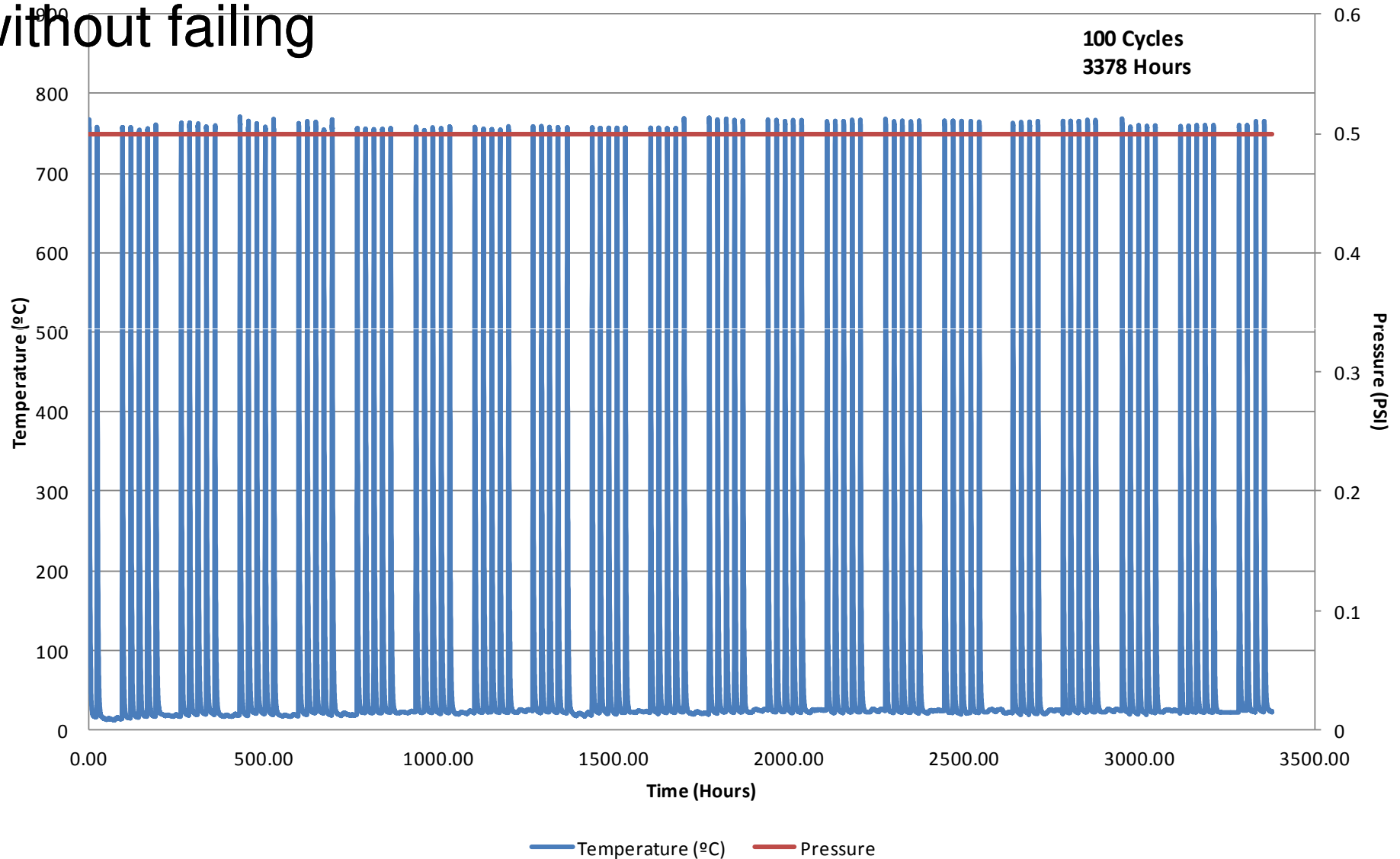
We have examined compositions with low liquidus temperatures in the Ba-borosilicate system

# Hermetic Sealing Tests



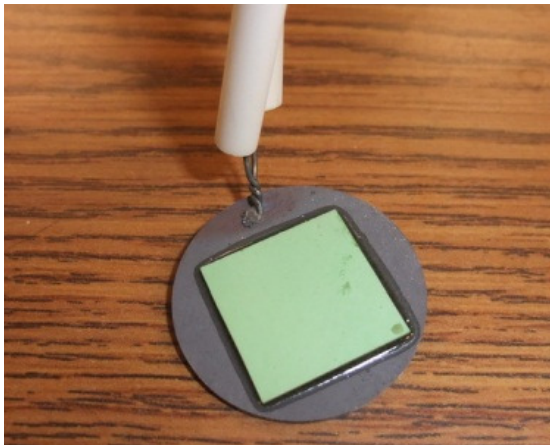
- Glass pastes were made from powders ( $-45\ \mu\text{m}$ ) mixed with PVB binder and acetone, and used to bond NiO/YSZ bi-layer to aluminized steel (SS441) substrate (materials from PNNL)
- Sandwich seals fired in air at  $850^\circ\text{C}$  for 8 hours

# Viscous seals survey >100 thermal cycles from 750° C without failing

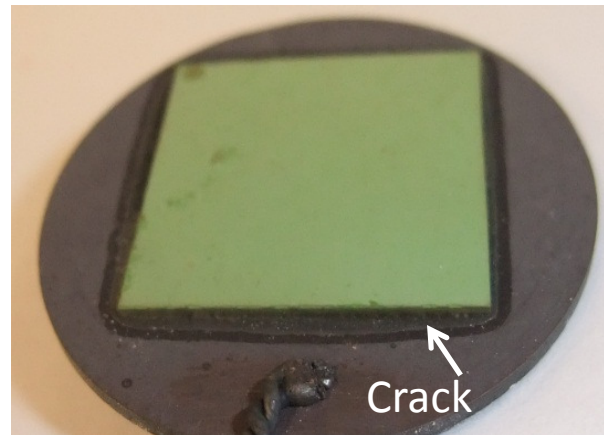


# Thermally shocked sample “re-seals” when re-heated

Original hermetic seal



Cracked on quenching  
( $>25^{\circ}$  C/s)



Resealed (2 hrs at  $725^{\circ}$  C)



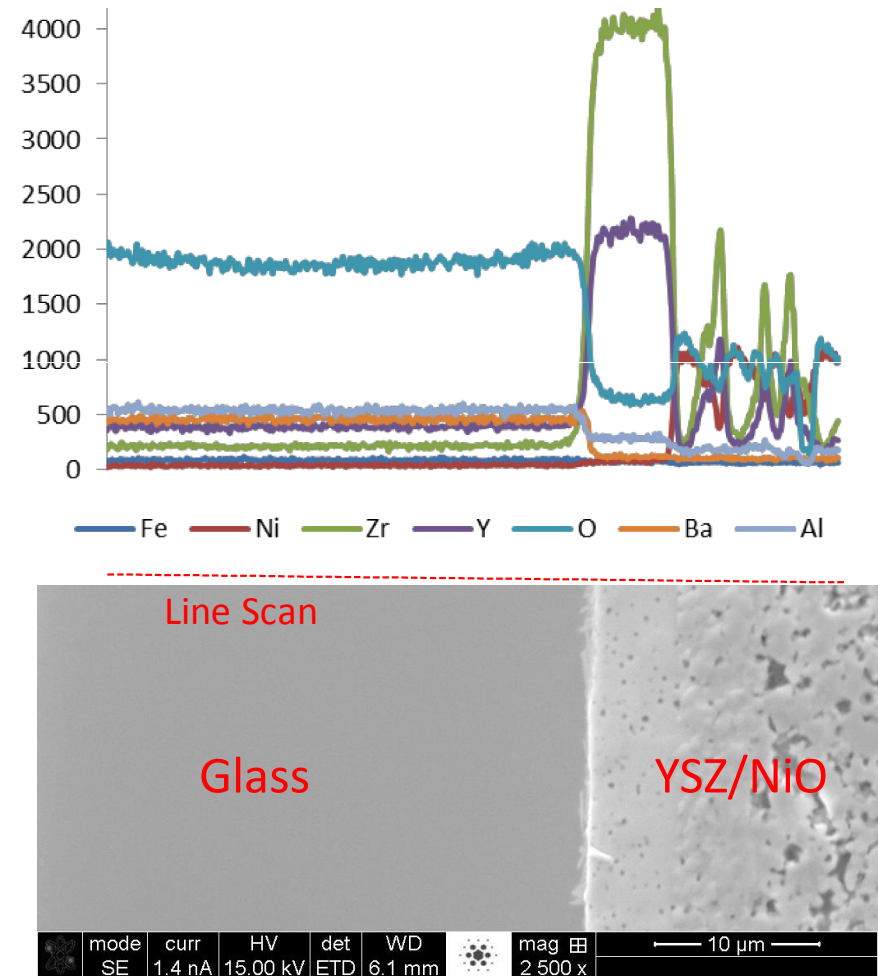
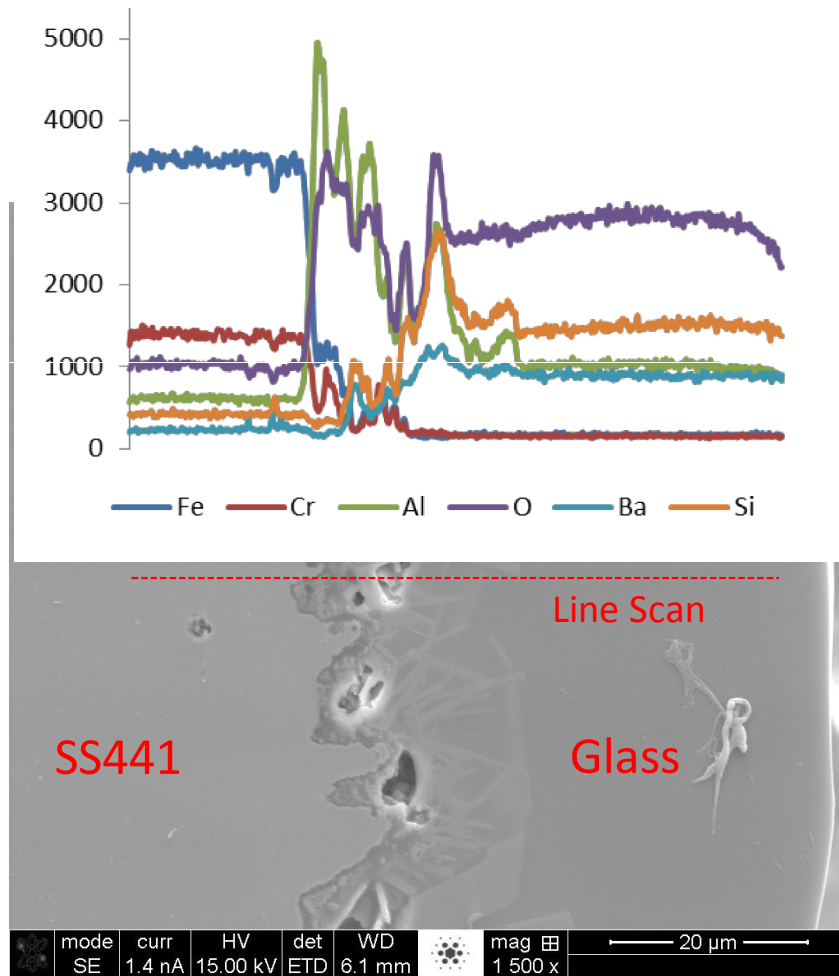
Foaming in soapy water



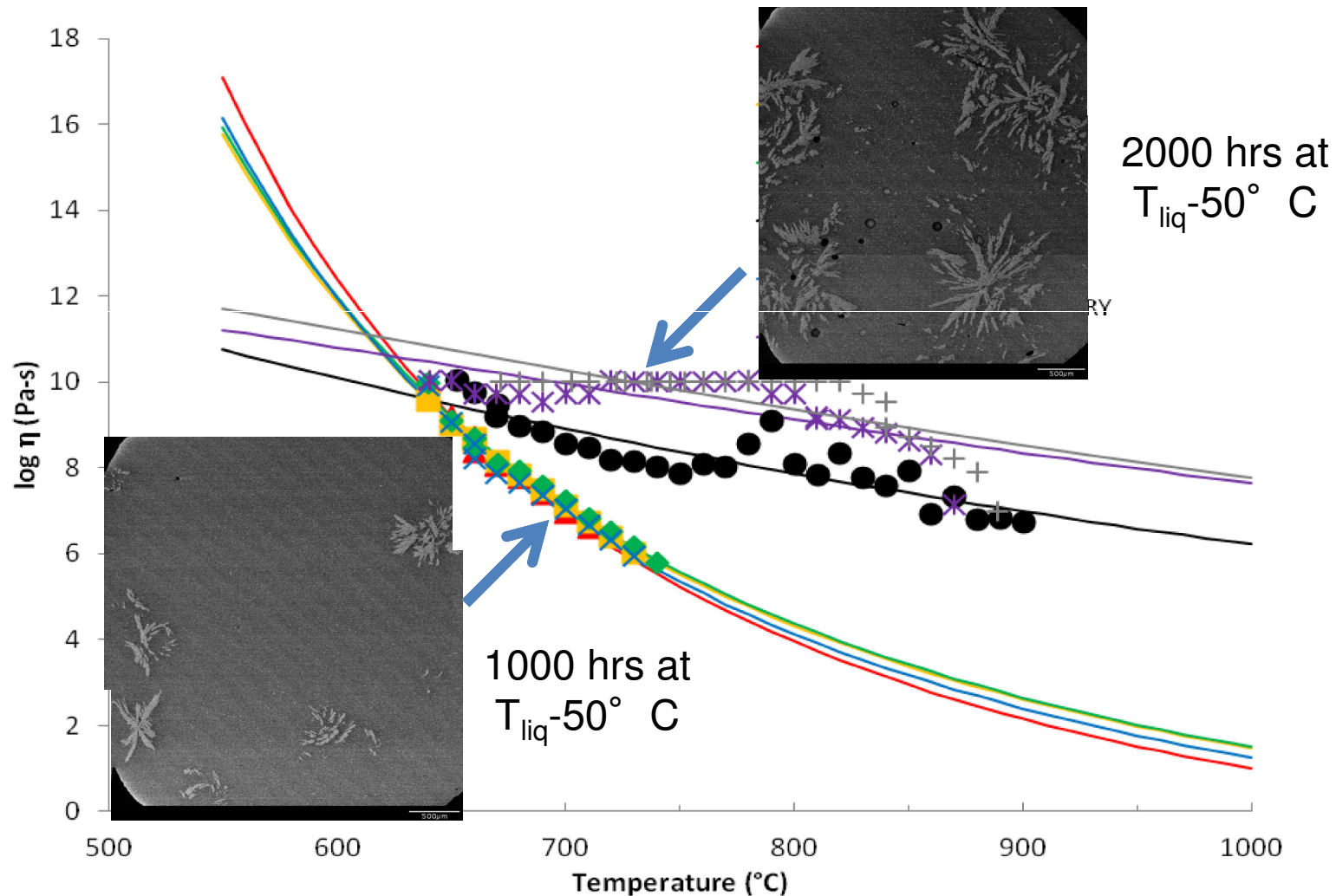
Samples re-seal in  
two hours with  
viscosities of  $10^6$  Pa-s



# Viscous seals may be more reactive than the glass-ceramics



Long-term crystallization will affect glass viscosity-  
and so the self-sealing properties



## Summary

- As a materials science platform, sealing glasses offer opportunities to explore new compositions and to study glass phenomena
  - Chemically stable non-silicate compositions
  - Crystallization around the liquidus temperature
  - High temperature compatibility with metals
- Glass seals are enabling materials for many technologies
  - Reliable Li-batteries → biomedical devices
  - Optimization still required for Na/S, Na/NiCl<sub>2</sub> and SOFC systems
- The ability to model sealing processes may be the key to 'scaling up' technologies to useful products
  - Accurate viscoelastic properties
  - Well-controlled manufacturing process parameters
  - Well-understood 'application' conditions

## Acknowledgments

- Department of Energy/SECA
  - Mo-Sci Corp. (Rolla)- CW Kim
  - Signo Reis, Teng Zhang, Rick Hsu
- National Institutes of Health
  - Laxikanth Peddi, Heather Teitlebaum, Roger Brown
- Sandia National Labs





A scenic photograph of a coastal town, likely in Sicily, with a large mountain (Mount Etna) visible in the background. The town is built on a hillside overlooking the sea. In the foreground, there are rocky cliffs and waves crashing against them. The word "Grazie!" is written in large white letters across the center of the image.

Grazie!